CoPP + microbes

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(54) Title: USE OF COPPER AND ZINC SILICATE FOR CONTROLLING MICROBES

(57) Abstract: A method for controlling microbes comprising the step of contacting said microbes with an effective amount of copper silicate and zinc silicate.

Use of Copper Silicate and Zinc Silicate for Controlling Microbes

Field of the Invention

The present invention relates to the use of a combination of copper silicate and zinc silicate as a bactericide/fungicide for non-medical applications. The present invention also relates to a copper/zinc silicate composition and to the use of such a composition as a plant bactericide/fungicide for non-medical applications.

Background Art

Anti-microbial compositions such as fungicides and bactericides are either chemical or biological agents that are used to control microbes in a variety of non-medical environments.

In agriculture, antimicrobials are used to protect crops from pests, such as infectious pathogens that, if left uncontrolled, result in the weakening or destruction of a plant. In regards to agricultural crops, this is unacceptable, as economic losses will result. To protect valuable agricultural crops, it is desired to have an anti-microbial composition that readily eliminates or treats various plant maladies as well as other infectious diseases without undue toxicity or other undesirable effects.

Currently, agricultural antimicrobials based on copper or other metals are typically applied either as a dispersed solid (for example copper oxychloride or copper hydroxide) or as a soluble solution (for example copper sulphate).

Application of dispersed solids requires that the solids be presented as fine powder and the fineness of the powder dictates the coverage of the active component upon application. The finer the powder the more even the active component is distributed. However, fine powders lead to dustiness causing environmental and health issues associated with inhalation of the product and/or clumping that results in equipment blockages and hampers the application of the product. Some of these problems can be reduced by using dispersants and other

additives however these complicate the manufacturing process and ultimately the efficacy of the product is still limited to the particle size of the active agent.

Antimicrobial solutions containing active agents, such as copper or zinc, in soluble form do not have the same problems. However, the nature of standard soluble products is such that after application, the dried active agent is able to be resolubilised and thus can be lost from the original location of application through contact with water or some other fluid.

The Applicants have previously produced a soluble copper silicate product (see US 5,474,972) that is suitable for use against a variety of pests such as snails and slugs and overcomes a number of the problems discussed above associated with antimicrobial solutions and dispersed solids. Soluble zinc silicate on the other hand is not known as a bactericide or fungicide.

Soluble copper silicate and zinc silicate have not been used together for antimicrobial purposes. Furthermore, to date no single formulation containing copper silicate and zinc silicate in soluble form has been produced or used as an antimicrobial. The present invention seeks to overcome or at least partially alleviate this deficiency by providing an improved copper/zinc silicate formulation and methods of using a combination of soluble copper silicate and zinc silicate as an antimicrobial.

Summary of the Invention

Unless stated to the contrary herein, the present invention relates to methods and compositions for use in non-medical applications such as agriculture and industrial uses.

The present invention provides a method of controlling microbes, such as bacteria and fungi, the method comprising the step of administering to said microbes an effective amount of soluble copper silicate and soluble zinc silicate.

The present invention also provides a combined copper silicate and zinc silicate composition effective in treating or preventing microbial infections. The composition includes those adapted for administration.

Brief description of the Figures

Figure 1 is a set of photographs illustrating the infection rating guidelines used in the examples;

Figure 2 is a graph illustrating disease development of tomato seedlings 2 days after infection with *B cinerea* and prior to any treatment. Disease development is measured as an average of plants within a single treatment group and using the guidelines in Figure 1. Disease development was measured on individual plants by taking measurements across various leaf levels (tip to L10). Typically lower leaves, L8/9, show signs of disease and/or wilting with or without infection due to natural growth patterns.

Figure 3 is a graph illustrating average disease development of tomato seedlings 7 days after initial infection with *B cinerea* and 5 days after treatment according to the present invention and a range of comparator formulations;

Figure 4 is a graph illustrating average disease development in plants pre-treated with a composition according to the present invention and a range of comparator formulations 3 days prior to inoculation;

Figure 5a is a graph illustrating the average protective action of compositions of the present invention relative to comparator formulations where treatment was undertaken on a weekly basis for 4 weeks prior to infection;

Figure 5b is a graph also illustrating the average protective action of compositions of the present invention relative to comparator formulations where treatment was undertaken on a weekly basis for 4 weeks prior to infection;

Figure 6a is a graph illustrating average the protective action of compositions of the present invention relative to comparator formulations where treatment was undertaken twice on a fortnightly basis prior to infection;

Figure 6b is a graph also illustrating the average protective action of compositions of the present invention where treatment was undertaken twice on a fortnightly basis prior to infection;

Figure 7 is a graph illustrating the average protective action of compositions of the present invention relative to comparator formulations where treatment was undertaken once only, 4 weeks prior to infection;

Figure 8 is a graph illustrating the average infection rating of plants pretreated weekly (4 applications) with various active agents and then challenged with *Botrytis* 2 days after the last pretreatment;

Figure 9 is a graph illustrating the average infection rating of plants pretreated weekly (4 applications) with various active agents and then challenged with *Botrytis* 2 days after the last pretreatment;

Figure 10 is a graph illustrating the average infection rating of plants pretreated fortnightly (2 applications) with various active agents and then challenged with *Botrytis* 23 days after the initial application;

Figure 11 is a graph illustrating the average infection rating of plants pretreated fortnightly (2 applications) with various active agents and then challenged with *Botrytis* 23 days after the initial application;

Figure 12 is a graph illustrating the average infection rating of plants pretreated once with various active agents and then challenged with *Botrytis* 23 days after the initial application;

Figure 13 is a graph illustrating the average infection rating of plants treated once with various active agents after infection with *Botrytis*;

Figure 14 is a graph illustrating the average infection rating of plants pretreated once with various active agents and then challenged with *Botrytis* three days later;

Figure 15 is a graph illustrating the average infection rating of plants pretreated once with various active agents and then challenged with *Botrytis* three days later

Figure 16 is a graph illustrating the decreased phytotoxicity of agents of the present invention relative to copper silicate solutions when applied to grape vines;

Figure 17 is a graph illustrating the decreased phytotoxicity of agents of the present invention relative to copper silicate solutions when applied to potatoes using "percent of leaves with phytotoxic symptoms" as the measure of phytotoxicity; and

Figure 18 is a graph illustrating the decreased phytotoxicity of agents of the present invention relative to copper silicate solutions when applied to potatoes using "mean phytotoxic impact per leaf" as the measure of phytotoxicity.

Detailed description of the Invention

Methods of controlling microbes

The present invention provides a method for controlling microbes, such as bacteria and fungi, the method comprising the step of administering to said microbes an effective amount of soluble copper silicate and soluble zinc silicate.

The present invention is based on the surprising discovery that the use of soluble copper silicate and zinc silicate in combination is more effective than when they are used separately. In this regard, it appears there is a synergistic effect obtained when the soluble silicates are used together.

Throughout this specification, unless the context requires otherwise, the word "comprise", or variations such as "comprises" or "comprising" will be understood to imply the inclusion of a stated integer or group of integers, but not the exclusion of any other integer or group of integers including method steps.

Throughout this specification, unless the context requires otherwise, the word "control", or variations such as "controls" or "controlling", when used in relation to methods involving the administration of an agent(s) to an environment containing a microbe, will be understood to encompass the inhibition of microbial growth and the killing of microbes.

The method of the present invention may be applied to plants. When the method is applied to plants to control microbial infection thereon, various types of plants may be subjected to the method of the present invention including crops and domestic plants.

The present invention also provides a method for preventing microbial growth, such as bacteria and fungi, the method comprising the step of administering to an environment with a potential to contain the microbes an effective amount of soluble copper silicate and soluble zinc silicate.

The methods of the present invention may be applied to control or prevent the growth of a range of microbes including plant pathogens such as one or more microbes selected from the group comprising *Botrytis. spp* such as, *B. squamosa, B. tulipae, B fabae* and *B cinerea; Legionella spp; Aschocyts spp such as A rabiei* and *A lentis; Altenaria spp* such as *Altenaria altenata; Colletotrichum spp and Colleotrichum spp* such as *C gloeosporoides.*

Preferably, the method of the present invention controls the microbes by at least inhibiting their growth and even more preferably totally preventing their growth. In this regard, the zinc and copper silicate may act as a bacteriostatic or fungistatic agent. Alternatively, the zinc silicate and copper silicate administered according to the method of the present invention may be lethal to the microbes and thus act as a bactericide or fungicide. Whether the zinc and copper silicate acts to inhibit growth or kills the microbes depends at least partially on the amount of zinc and copper silicate administered and the medium in which the microbe is located. A skilled person may determine effective dosages of the zinc silicate and copper silicate for particular applications.

The mode of action of the compositions of the present invention is varied and includes acting as a systemic agent as well as a topical agent.

The form of the copper silicate and zinc silicate combination may be varied insofar as the silicates may be applied as separate components or as a single mixture. When the silicates are applied as separate components they may be added sequentially or simultaneously provided they are applied in a fashion that allows for the enhanced cumulative effect to be obtained. Alternatively and preferably, they are combined and applied as a single mixture.

As mentioned above, the effective amount of copper silicate may be varied depending on the particular application. When the copper silicate is in the form of an aqueous solution of acidified copper silicate, such as the copper silicate in US 5,474,972, the effective amount of copper silicate may be to a final concentration of approximately 0.04 g/L - 1.4g/L, 0.1 g/L – 1 g/L or 0.3 to 0.8 g/L (as Cu). Preferably, the effective amount of copper silicate is to a final concentration of approximately 0.56g/L (as Cu).

The effective amount of zinc silicate may be varied depending on the particular application. When the zinc silicate is in the form of an aqueous solution, the effective amount of zinc silicate may be to a final concentration of approximately 0.04 g/L - 1.4g/L, 0.1 g/L – 1 g/L or 0.3 to 0.8 g/L (as Zn). Preferably, the effective amount of zinc silicate is to a final concentration of approximately 0.56g/L (as Zn).

Preferably, the ratio of copper (final concentration) to zinc (final concentration) is 1:1 i.e. equal. Alternatively, the ratio may be between approximately 40:1 and 1:40 such as, 1:20 or 20:1, 1:10 or 10:1, 1:4 or 4:1, 1:3 or 3:1.

The effective amounts of combination of zinc silicate and copper silicate may be determined by one of ordinary skill in the art without undue experimentation using appropriate *in situ* and *in vitro* experiments.

The silicate composition(s) may be applied in the method of the present invention in various forms and preferably comprises an aqueous solution of acidified copper

silicate. The acidified copper silicate solution is especially preferred in the method of the present invention as it has a number of advantages when compared to other copper compounds. These include: (i) persistent toxicity when compared to insoluble copper powders; and (ii) ease of application.

Preferably, the zinc silicate applied in the method of the present invention comprises an aqueous solution of acidified zinc silicate. The acidified zinc silicate solution is especially preferred in the method of the present invention as it has a number of advantages when compared to other zinc compounds. These include: (i) persistent toxicity when compared to insoluble zinc powders; and (ii) ease of application.

When the copper silicate and zinc silicate is applied as a single liquid mixture the mixture is preferably in a form where the silicate components are soluble. This may be achieved by preparing the zinc and copper solutions separately and then combining them to make the single liquid mixture. Preferably, the copper silicate solutions are produced according to the methods in US 5474972. Surprisingly, it has been found by substituting the copper salts with zinc salts the methods in US 5474972 can also be used to produce the zinc silicate solutions.

The mode of applying the solutions of the present invention may be varied depending on the particular site to which the solution is to be applied. For example, the solutions of the present invention may be conveniently applied by spraying on to the leaves or stems of plants.

Methods of preparing a copper silicate and zinc silicate composition

The present invention also provides a method of producing a copper silicate and zinc silicate composition, the method comprising the steps of:

(i) reacting a copper salt with an alkali silicate in an acidic solvent to produce an aqueous solution of acidified copper silicate; and

(ii) reacting a zinc salt with an alkali silicate in an acidic solvent to produce an aqueous solution of acidified copper silicate; and

(iii) combining the products of (i) and (ii) to form the composition.

The manner in which the products of (i) and (ii) above are combined may be varied as required. For example, steps (i) and (ii) may be carried out independently and then the respective products added together to form the composition. Thus, step (iii) may comprise mixing the solutions from steps (i) and (ii).

Alternatively, the reactions identified in steps (i) (ii) and (iii) can be carried out simultaneously by combining the salts, the silicate and the solvent together in a single reaction vessel. Thus, the present invention also provides a method of producing a copper silicate and zinc silicate composition, the method comprising the steps of:

(i) reacting a copper salt with an alkali silicate in an acidic solvent to produce an aqueous solution of acidified copper silicate; and

(ii) reacting a zinc salt with an alkali silicate in an acidic solvent to produce an aqueous solution of acidified zinc silicate; wherein steps (i) and (ii) are carried out simultaneously in a single reaction vessel to form the composition.

According to another alternative, each salt can be reacted with the acidic solvent and combined together before being reacted with the alkali silicate to form the composition. Thus, the present invention also provides a method of producing a copper silicate and zinc silicate composition, the method comprising the steps of:

(i) reacting a copper salt with an acidic solvent;

(ii) reacting a zinc salt with an acidic solvent; and

(iii) reacting the products from (i) and (ii) with an alkali silicate to form the composition.

Preferably, the acidic solvent buffers the mixture of the salts and alkali silicate such that the acidified copper silicate and zinc silicate has a pH in the range of 2 to 6 and more preferably in the range of 3 to 5. Even more preferably, the salt is dissolved prior to reaction with the alkali silicate.

The acidic solvent may be varied and includes a mixture of acetic acid and sodium acetate. When the solvent is acetic acid and sodium acetate they may be provided in a ratio of between 1:5 and 5:1 and in a concentration of 0.01 to 10% w/w.

The salts may be varied and include sulphates, oxides, hydroxides and chlorides. Examples of sulphates include sulphate pentahydrate (for copper only) and sulphate monohydrate and heptahydrate (for zinc only). Depending on the salt used the amount of acid required to effectively buffer the composition as a solution may vary. The amount of the relative reactants can be routinely determined by a skilled person. When the salt is copper sulphate pentahydrate it may be present in an amount in the range of 0.1 to 25% w/w.

The alkali silicate may also be varied and includes sodium silicate. When sodium silicate is used it may have a ratio of SiO_2 to Na_2O of from 3.75:1 to 1:2, and may be present in an amount in the range of 0.05 to 20% w/w.

In all of the above methods water may be used to dilute one or more of the reactants.

The present invention also extends to compositions prepared according to the above methods.

Copper silicate and zinc silicate Compositions

The present invention also provides compositions comprising copper silicate and zinc silicate in amounts effective to control microbes. It will be appreciated that

the precise amounts of copper silicate and zinc silicate in the compositions may vary depending on the particular end use. Preferably, the effective amount of each silicate is to a final concentration of approximately 0.04 g/L - 1.4g/L, 0.1 g/L – 1 g/L or 0.3 to 0.8 g/L (as Cu or Zn). In one particular form of the invention the effective amount of each silicate is 0.56g/L (as Cu or Zn).

Thus, it will be appreciated that the ratio of copper silicate to zinc silicate in the compositions may be varied. Preferably, the ratio of copper (final concentration) to zinc (final concentration) is 1:1 i.e. equal. Alternatively, the ratio may be between approximately 40:1 and 1:40 such as, 1:20 or 20:1, 1:10 or 10:1, 1:4 or 4:1, 1:3 or 3:1.

Topical Formulations

The copper silicate and zinc silicate may be provided in a form that is adapted for topical application. Various topical delivery systems may be appropriate for administering the compositions of the present invention depending upon the preferred treatment regimen. Topical formulations may be produced by dissolving or combining the copper silicate and zinc silicate in an aqueous or non-aqueous carrier. In general, any liquid, cream, or gel, or similar substance that does not appreciably react with the copper or zinc silicate or any other active ingredient that may be introduced and which is non-irritating is suitable.

Suitable formulations are well known to those skilled in the art and include, but are not limited to, solutions, suspensions, emulsions, creams, gels, ointments, powders, liniments, salves and transdermal patches, etc, which are, if desired, sterilized or mixed with auxiliary agents, e.g., preservatives, stabilizers, emulsifiers, wetting agents, fragrances, colouring agents, odour controllers, thickeners such as natural gums etc. Particularly preferred topical formulations include ointments, creams or gels.

Ointments generally are prepared using either (1) an oleaginous base, i.e., one consisting of fixed oils or hydrocarbons, such as white petroleum or mineral oil, or (2) an absorbent base, i.e., one consisting of an anhydrous substance or substances which can absorb water, for example anhydrous lanolin. Customarily,

following formation of the base, whether oleaginous or absorbent, the active ingredient is added to an amount affording the desired concentration.

Creams are oil/water emulsions. They consist of an oil phase (internal phase), comprising typically fixed oils, hydrocarbons and the like, waxes, petroleum, mineral oil and the like and an aqueous phase (continuous phase), comprising water and any water-soluble substances, such as added salts. The two phases are stabilised by use of an emulsifying agent, for example, a surface active agent, such as sodium lauryl sulfate; hydrophilic colloids, such as acacia colloidal clays, veegum and the like. Copper silicate and zinc silicate are customarily added to the water phase prior to formation of the emulsion, in an amount to achieve the desired concentration.

Gels comprise a base selected from an oleaginous base, water, or an emulsion-suspension base. To the base is added a gelling agent that forms a matrix in the base, increasing its viscosity. Examples of gelling agents are hydroxypropyl cellulose, acrylic acid polymers and the like. Customarily, the copper and zinc is added to the formulation at the desired concentration at a point preceding addition of the gelling agent.

The amount of compound incorporated into a topical formulation is not critical; the concentration should be within a range sufficient to permit ready application of the formulation to the affected tissue area in an amount that will deliver the desired amount of copper silicate and zinc silicate to the desired treatment site.

The customary amount of a topical formulation to be applied to an affected tissue will depend upon an affected tissue size and concentration of the active components in the formulation.

<u>Methods of Treatment</u>

The present invention also provides a method for treating a microbial infection, which method comprises the step of: contacting a copper silicate and zinc silicate composition as herein described with the infection for sufficient time to substantially remove or control the infection.

It will be appreciated that the composition may be given as a single dose schedule, or more preferably, in a multiple dose schedule. A multiple dose schedule is one in which a primary course of delivery may be with 1 to 100 separate doses, followed by other doses given at subsequent time intervals required to maintain or reinforce the treatment. The dosage regimen will also, at least in part, be determined by the judgement of the user.

Further features of the present invention are more fully described in the following non-limiting examples. It is to be understood that this detailed description is included solely for the purpose of exemplifying the present invention. It should not be understood in any way as a restriction on the broad description of the invention as set out above.

Examples

Example 1 – Control of bacterial and fungal pathogens *in vitro.*

Materials and Methods

A series of microtitre plates containing a number of individual wells were set up as shown in table 1.1 with each well containing 100µl of malt extract broth, 50µl of the appropriate formulation and 50µl of inoculum solution containing 2.5×10^4 spores (colony forming units). The solutions listed should be read as "100%" solutions and the dilutions used in the individual well treatments are listed in the first column of Table 1.1. Individual plates were then maintained in an incubation cabinet under standard conditions for 5 days. After this time, the plates were removed and pathogen growth was assessed by visual observation compared to growth in untreated (water) wells. Minimum inhibitory concentration (MIC) was determined as the lowest concentration of solution where 75% or more reduction in growth versus the water standard was achieved. Four replicate plates were used for each pathogen tested. Average MIC data for tests are shown in Table 1.2.

Table 1.1 Microtitre plate arrangement and treatment concentrations for *in vitro* studies.

Solution (%)	Water	S100	CS100	ZS100	CZS 75/25	CZS 5050
50						
25						
12.5						
6.25						
3.125						
1.56						
0.78						
0						

S100 = Silicate solution containing 3.4% as SiO_2

CS100 = copper silicate solution containing 2.8g/L as Cu

ZS100 = zinc silicate solution containing 2.8g/L as Zn

CZS7525 = copper/zinc silicate solution containing 2.1g/L as Cu and 0.7g/L as Zn

CZS5050 = copper/zinc silicate solution containing 1.4g/L as Cu and 1.4g/L as Zn

Results

Extensive growth in all "water" treatments was observed. Copper silicate and zinc silicate formulations showed good control of pathogen growth at low concentrations (see table 1.2). However, combinations of copper silicate and zinc silicate consistently showed activity in controlling pathogen growth at concentrations equivalent to, or lower than that observed for either copper silicate alone or zinc silicate alone. This indicates greater activity of the mixed metal formulations in controlling pathogen growth.

Table 1.2. Minimum Inhibitory Concentration (% of original formulation) as determined by the average of 4 replicate plates for each pathogen.

	Pathogen			
Treatment	**B1**	**B2**	**B3**	**A1**
S100	>50	>50	>50	>50
CS100	4.69	3.13	9.38	1.56
ZS100	4.69	5.63	25.00	3.90
CZS7525	1.56	2.34	6.25	1.56
CZS5050	2.74	3.13	9.38	1.56

Key to Pathogens:

A1 = *Altenerea altenata*

B1 = *Botrytis cinerea* (strain #1)

B2 = *Botrytis cinerea* (strain #2)

B3 = *Botrytis fabae*

Example 2. The use of a combined copper silicate/zinc silicate composition for controlling *Botrytis* infection in a curative fashion.

Materials and Methods

A) Infection

Tomato seedlings were grown from seed and healthy specimens were selected 3 weeks after transplanting into 14cm plastic pots.

Seedlings were inoculated with *Botrytis cinerea* spores in an infection tent comprising a boxed trellis covered with plastic sheeting. The entire plant was covered with a spore suspension (containing 10^5 spores per ml) using an aerosol propelled spray pack.

on disease development. The most effective formulation was the copper silicate/zinc silicate mixture (CZS50:50).

After infection for 2 days (prior to treatments) all plant groups were approximately equally infected (Figure 2). All plants at this stage had experienced the same conditions – that is, infection with *B. cinerea* but no treatment. They are shown in Figure 2 in their treatment groups so as to distinguish the individual groups.

After infection development for 5 days the most effective treatment in reducing disease development was the combination of copper silicate and zinc silicate (CZS5050) (Figure 3.).

Example 3 - The use of a combined copper silicate/zinc silicate composition for preventing *Botrytis* infection

Materials and Method

Healthy tomato seedlings (var. Gross Lisse) approximately 25-30cm in height were selected for use in the experiment. Treatments used were:

(a) Copper silicate solution (1.12g/L as copper)

(b) Zinc silicate solution (1.12g/L as zinc)

(c) Copper/zinc silicate solution (0.56g/L as copper and 0.56g/L as zinc)

(d) Kocide (copper hydroxide) suspension (1g/L as copper)

Four plants were used as replicates for each treatment. Plants were sprayed with the various treatments and then after 3 days the plants were inoculated with a spore suspension of *Botrytis cinerea*. After inoculation, the plants were contained in a humid infection tent, in the dark, for 2 days to allow for disease development and were then returned to the glasshouse. After a further 5 days the level of disease development on each leaf was rated using a scale of 0-3.

Following infection, the plants were held in the tent for 2 days in the dark. Within the infection tent, temperatures ranged from 18-27°C and the humidity was stable at 100%.

B) Treatments

Seedlings were removed from the infection tent and infection development was recorded. The treatment solutions were then applied using a hand held pump spray apparatus. Individual plants were sprayed to run-off for all applications. Four specimens were used for each treatment:

(a) Untreated ("unsprayed") – infected plants not treated

(b) Treatment A ("CuOCl") – copper oxychloride solution 1.25g/L as Cu

(c) Treatment B ("CS100")- Copper silicate solution 1.4g/L as Cu

(d) Treatment C ("ZS100")- Zinc silicate solution 1.4g/L as Zn

(e) Treatment D (CZS50:50) - Copper/zinc silicate solution 0.7g/L as Cu and 0.7g/L as Zn

(f) Blank - Plants not infected and not treated

After treatment the plants were transferred to a heated glasshouse with regular overhead misting to maintain humid conditions. Within the humid glasshouse, temperatures ranged from 19-33°C and humidity from 60-90%. Disease development on each leaf was assessed when the seedlings were removed from the infection tent and 5 days after removal from the infection tent (i.e. 5 days after treatment and 7 days after initial inoculation.) Infection development was recorded by individual rating of each leaf using a standard half integer scale ranging from 0 to 3. Zero indicates no infection while 3 indicates the leaf is dead. Examples of disease rating are shown in Figure 1.

<u>Results</u>

Disease severity, (as measured by the average of leaf infection ratings for the four replicates of each treatment) was reduced, but not halted by CuOCl and the copper silicate (CS100) formulations. The zinc silicate (ZS100) had little impact

A series of plants (4 replicates) which were untreated (i.e. not sprayed) were subjected to inoculation and assessment and used for comparison as untreated samples.

Results

Average infection ratings are shown in Figure 4. Infection on the leaves treated with the copper/zinc combination product is generally less than that found for other treatments, and substantially less than for untreated samples and for the commercially available Kocide product. Generally, infection is worse in the lower leaves. Nonetheless, the mixed metal product is found to be generally more effective in preventing infection development than other silicate based products.

Example 4. The use of a combined copper silicate/zinc silicate composition for preventing *Botrytis* infection by weekly spray application.

Materials and Method

Healthy tomato seedlings (var. Gross Lisse) approximately 25-30cm in height were selected for use in the experiment. Treatments used were:

(a) Copper silicate solution (1.12g/L as copper)

(b) Zinc silicate solution (1.12g/L as zinc)

(c) Copper/zinc silicate solution (0.56g/L as copper and 0.56g/L as zinc)

(d) Kocide (copper hydroxide) suspension (1g/L as copper)

Four plants were used as replicates for each treatment. Plants were sprayed with treatments and were then resprayed with the same product after 7 days and again after 14 days and 21 days. (i.e. 4 spray applications at weekly intervals over a month.) Two days after the final spray application the plants were inoculated with a spore suspension of *Botrytis cinerea*. After inoculation, the plants were contained in a humid infection tent, in the dark, for 2 days to allow for disease

development and were then returned to the glasshouse. After a further 5 days the level of disease development on each leaf was rated using a scale of 0-3.

A series of plants of the same age (4 replicates) which were untreated (i.e. not sprayed) were subjected to inoculation and assessment and used for comparison as untreated samples.

Results

Average infection ratings are shown in Figure 5a. Infection on the leaves treated with the copper/zinc combination product is generally less than that found for other treatments.

Example 5. The use of a combined copper silicate/zinc silicate composition for preventing *Botrytis* infection by weekly spray application.

Materials and Method

This trial repeated the conditions and design carried out in example 4. Healthy tomato seedlings (var. Gross Lisse) approximately 25-30cm in height were selected for use in the experiment. Treatments used were:

(a) Copper silicate solution (1.12g/L as copper)

(b) Zinc silicate solution (1.12g/L as zinc)

(c) Copper/zinc silicate solution (0.56g/L as copper and 0.56g/L as zinc)

(d) Kocide (copper hydroxide) suspension (1g/L as copper)

Four plants were used as replicates for each treatment. Plants were sprayed with treatments and were then resprayed with the same product after 7 days and again after 14 days and 21 days. (i.e. 4 spray applications at weekly intervals over a month.) Two days after the final spray application the plants were inoculated with a spore suspension of *Botrytis cinerea*. After inoculation, the plants were

contained in a humid infection tent, in the dark, for 2 days to allow for disease development and were then returned to the glasshouse. After a further 5 days the level of disease development on each leaf was rated using a scale of 0-3.

A series of plants of the same age (4 replicates) which were untreated (i.e. not sprayed) were subjected to inoculation and assessment and used for comparison as untreated samples.

Results

Average infection rating is shown in Figure 5b. Infection on the leaves treated with the copper/zinc combination product is generally less than that found for other treatments.

Example 6. The use of a combined copper silicate/zinc silicate composition for preventing *Botrytis* infection by fortnightly spray application.

Materials and Method

Healthy tomato seedlings (var. Gross Lisse) approximately 25-30cm in height were selected for use in the experiment. Treatments used were:

(a) Copper silicate solution (1.12g/L as copper)

(b) Zinc silicate solution (1.12g/L as zinc)

(c) Copper/zinc silicate solution (0.56g/L as copper and 0.56g/L as zinc)

(d) Kocide (copper hydroxide) suspension (1g/L as copper)

Four plants were used as replicates for each treatment. Plants were sprayed with treatments and were then resprayed with the same product after 14 days. After a further 9 days (i.e. 23 days after the initial spray) the plants were inoculated with a spore suspension of *Botrytis cinerea*. After inoculation, the plants were contained in a humid infection tent, in the dark, for 2 days to allow for disease development

and were then returned to the glasshouse. After a further 5 days the level of disease development on each leaf was rated using a scale of 0-3.

A series of plants of the same age (4 replicates) which were untreated (i.e. not sprayed) were subjected to inoculation and assessment and used for comparison as untreated samples.

Results

Average infection rating is shown in Figure 6a. Infection on the leaves treated with the copper/zinc combination product is generally less than that found for other treatments.

Example 7. The use of a combined copper silicate/zinc silicate composition for preventing *Botrytis* infection by fortnightly spray application.

Materials and Method

This trial repeated the conditions and design carried out in example 6. Healthy tomato seedlings (var. Gross Lisse) approximately 25-30cm in height were selected for use in the experiment. Treatments used were:

(a) Copper silicate solution (1.12g/L as copper)

(b) Zinc silicate solution (1.12g/L as zinc)

(c) Copper/zinc silicate solution (0.56g/L as copper and 0.56g/L as zinc)

(d) Kocide (copper hydroxide) suspension (1g/L as copper)

Four plants were used as replicates for each treatment. Plants were sprayed with treatments and were then resprayed with the same product after 14 days. After a further 9 days (i.e. 23 days after the initial spray) the plants were inoculated with a spore suspension of *Botrytis cinerea*. After inoculation, the plants were contained in a humid infection tent, in the dark, for 2 days to allow for disease development

and were then returned to the glasshouse. After a further 5 days the level of disease development on each leaf was rated using a scale of 0-3.

A series of plants of the same age (4 replicates) which were untreated (i.e. not sprayed) were subjected to inoculation and assessment and used for comparison as untreated samples.

Results

Average infection rating is shown in Figure 6b. Infection on the leaves treated with the copper/zinc combination product is generally less than that found for other treatments.

Example 8. The use of a combined copper silicate/zinc silicate composition for preventing *Botrytis* infection by one monthly spray application.

Materials and Method

Healthy tomato seedlings (var. Gross Lisse) approximately 25-30cm in height were selected for use in the experiment. Treatments used were:

(a) Copper silicate solution (1.12g/L as copper)

(b) Zinc silicate solution (1.12g/L as zinc)

(c) Copper/zinc silicate solution (0.56g/L as copper and 0.56g/L as zinc)

(d) Kocide (copper hydroxide) suspension (1g/L as copper)

Four plants were used as replicates for each treatment. Plants were sprayed with treatments and then 23 days after application the plants were inoculated with a spore suspension of *Botrytis cinerea*. After inoculation, the plants were contained in a humid infection tent, in the dark, for 2 days to allow for disease development and were then returned to the glasshouse. After a further 5 days the level of disease development on each leaf was rated using a scale of 0-3.

A series of plants of the same age (4 replicates) which were untreated (i.e. not sprayed) were subjected to inoculation and assessment and used for comparison as untreated samples.

Results

Average infection ratings are shown in Figure 7. Infection on the leaves treated with the copper/zinc combination product is generally less than that found for other treatments.

Example 9A - The use of a combined copper silicate/zinc silicate composition for preventing *Botrytis* infection by weekly spray application

Materials and Method

Healthy tomato seedlings (var. Gross Lisse) approximately 25-30cm in height were selected for use in the experiment. Treatments used were:

(a) Copper silicate solution (1.12g/L as copper)

(b) Zinc silicate solution (1.12g/L as zinc)

(c) Copper/zinc silicate solution (0.56g as copper and 0.56g as zinc)

(d) Kocide (copper hydroxide) suspension (1g/L as copper)

Four plants were used as replicates for each treatment. Plants were sprayed with treatments and were then resprayed with the same product after 7 days and again after 14 days and 21 days. (*i.e.* 4 spray applications at weekly intervals over a month.) Two days after the final spray application the plants were inoculated with a spore suspension of *Botrytis cinerea*. After inoculation, the plants were contained in a humid infection tent, in the dark, for 2 days to allow for disease development and were then returned to the glasshouse. After a further 5 days the level of disease development on each leaf was rated using a scale of 0-3.

A series of plants of the same age (4 replicates) which were untreated (i.e. not sprayed) were subjected to inoculation and assessment and used for comparison as untreated samples.

Results

Average infection rating for each leaf level on the replicates are shown in Figure 8. Infection on the leaves treated with the copper/zinc combination product is generally less than that found for other treatments.

Example 9B - The use of a combined copper silicate/zinc silicate composition for preventing *Botrytis* infection by weekly spray application

Materials and Method

Healthy tomato seedlings (var. Gross Lisse) approximately 25-30cm in height were selected for use in the experiment. Treatments used were:

(a) Copper silicate solution (1.12g/L as copper)

(b) Zinc silicate solution (1.12g/L as zinc)

(c) Copper/zinc silicate solution (0.56g as copper and 0.56g as zinc)

(d) Kocide (copper hydroxide) suspension (1g/L as copper)

Four plants were used as replicates for each treatment. Plants were sprayed with treatments and were then resprayed with the same product after 7 days and again after 14 days and 21 days. (i.e. 4 spray applications at weekly intervals over a month.) Two days after the final spray application the plants were inoculated with a spore suspension of *Botrytis cinerea*. After inoculation, the plants were contained in a humid infection tent, in the dark, for 2 days to allow for disease development and were then returned to the glasshouse. After a further 5 days the level of disease development on each leaf was rated using a scale of 0-3.

A series of plants of the same age (4 replicates) which were untreated (*i.e.* not sprayed) were subjected to inoculation and assessment and used for comparison as untreated samples.

Results

Average infection rating for each leaf level on the replicates are shown in Figure 9. Infection on the leaves treated with the copper/zinc combination product is generally less than that found for either copper silicate or zinc silicate alone.

Example 9C - The use of a combined copper silicate/zinc silicate composition for preventing *Botrytis* infection by fortnightly spray application

Materials and Method

Healthy tomato seedlings (var. Gross Lisse) approximately 25-30cm in height were selected for use in the experiment. Treatments used were:

(a) Copper silicate solution (1.12g/L as copper)

(b) Zinc silicate solution (1.12g/L as zinc)

(c) Copper/zinc silicate solution (0.56g as copper and 0.56g as zinc)

(d) Kocide (copper hydroxide) suspension (1g/L as copper)

Four plants were used as replicates for each treatment. Plants were sprayed with treatments and were then resprayed with the same product after 14 days. Twenty three days after the initial spray application the plants were inoculated with a spore suspension of *Botrytis cinerea*. After inoculation, the plants were contained in a humid infection tent, in the dark, for 2 days to allow for disease development and were then returned to the glasshouse. After a further 5 days the level of disease development on each leaf was rated using a scale of 0-3.

A series of plants of the same age (4 replicates) which were untreated (i.e. not sprayed) were subjected to inoculation and assessment and used for comparison as untreated samples.

Results

Average infection rating for each leaf level on the replicates are shown in Figure 10. Infection on the leaves treated with the copper/zinc combination product is generally less than that found for other treatments.

Example 9D - The use of a combined copper silicate/zinc silicate composition for preventing *Botrytis* infection by fortnightly spray application

Materials and Method

Healthy tomato seedlings (var. Gross Lisse) approximately 25-30cm in height were selected for use in the experiment. Treatments used were:

(i) Copper silicate solution (1.12g/L as copper)

(ii) Zinc silicate solution (1.12g/L as zinc)

(iii) Copper/zinc silicate solution (0.56g as copper and 0.56g as zinc)

(iv) Kocide (copper hydroxide) suspension (1g/L as copper)

Four plants were used as replicates for each treatment. Plants were sprayed with treatments and were then resprayed with the same product after 14 days. Twenty three days after the initial spray application the plants were inoculated with a spore suspension of *Botrytis cinerea*. After inoculation, the plants were contained in a humid infection tent, in the dark, for 2 days to allow for disease development and were then returned to the glasshouse. After a further 5 days the level of disease development on each leaf was rated using a scale of 0-3.

A series of plants of the same age (4 replicates) which were untreated (i.e. not sprayed) were subjected to inoculation and assessment and used for comparison as untreated samples.

Results

Average infection rating for each leaf level on the replicates are shown in Figure 11. Infection on the leaves treated with the copper/zinc combination product is generally less than that found for either copper silicate or zinc silicate alone.

Example 9E - The use of a combined copper silicate/zinc silicate composition for preventing *Botrytis* infection by fortnightly spray application

Materials and Method

Healthy tomato seedlings (var. Gross Lisse) approximately 25-30cm in height were selected for use in the experiment. Treatments used were:

(i) Copper silicate solution (1.12g/L as copper)

(ii) Zinc silicate solution (1.12g/L as zinc)

(iii) Copper/zinc silicate solution (0.56g as copper and 0.56g as zinc)

(iv) Kocide (copper hydroxide) suspension (1g/L as copper)

Four plants were used as replicates for each treatment. Plants were sprayed with treatments and then, twenty three days after the initial spray application the plants were inoculated with a spore suspension of *Botrytis cinerea*. After inoculation, the plants were contained in a humid infection tent, in the dark, for 2 days to allow for disease development and were then returned to the glasshouse. After a further 5 days the level of disease development on each leaf was rated using a scale of 0-3.

A series of plants of the same age (4 replicates) which were untreated (i.e. not sprayed) were subjected to inoculation and assessment and used for comparison as untreated samples.

Results

Average infection rating for each leaf level on the replicates are shown in Figure 12. Infection on the leaves treated with the copper/zinc combination product is generally less than that found for other treatments.

Example 9F - The use of a combined copper silicate/zinc silicate composition for controlling a *Botrytis cinerea* infection in a curative fashion.

Materials and Methods

A) Infection

Tomato seedlings were grown from seed and healthy specimens were selected 3 weeks after transplanting into 14cm plastic pots.

Seedlings were inoculated with *B cinerea* spores in an infection tent comprising a boxed trellis covered with plastic sheeting. The entire plant was covered with a spore suspension (containing 10^5 spores per ml) using an aerosol propelled spray pack.

Following infection, the plants were held in the tent for 2 days in the dark. Within the infection tent, temperatures ranged from 18-27°C and the humidity was stable at 100%.

B) Treatments

Seedlings were removed from the infection tent and the treatment solutions were then applied using a hand held pump spray apparatus. Individual plants were sprayed to run-off for all applications.

Four specimens were used for each treatment:

(a) Untreated ("unsprayed") – infected plants not treated

(b) Treatment B ("CS100")- Copper silicate solution 1.4g/L as Cu

(c) Treatment C ("ZS100")- Zinc silicate solution 1.4g/L as Zn

(d) Treatment D (CZS50:50) - Copper/zinc silicate solution 0.7g/L as Cu and 0.7g/L as Zn

After treatment the plants were transferred to a heated glasshouse with regular overhead misting to maintain humid conditions. Within the humid glasshouse, temperatures ranged from 19-33°C and humidity from 60-90%. Disease development on each leaf was assessed 5 days after removal from the infection tent (i.e. 5 days after treatment and 7 days after initial inoculation.) Infection development was recorded by individual rating of each leaf using a standard half integer scale ranging from 0 to 3. Zero indicates no infection while 3 indicates the leaf is dead.

Results

Results are shown in Figure 13. The most effective treatment in reducing disease development was the combination of copper and zinc silicates (CZS5050).

Example 9G - The use of a combined copper silicate/zinc silicate composition for preventing *Botrytis* infection by spray application

Materials and Method

Healthy tomato seedlings (var. Gross Lisse) approximately 25-30cm in height were selected for use in the experiment. Treatments used were:

(a) Copper silicate solution (0.32g/L as copper)

(b) Zinc silicate solution (0.32g/L as zinc)

(c) Copper/zinc silicate solution (0.16g/L as copper and 0.16g/L as zinc)

Four plants were used as replicates for each treatment. Plants were sprayed with treatments and then, 3 days after the initial spray application the plants were inoculated with a spore suspension of *Botrytis cinerea*. After inoculation, the

plants were contained in a humid infection tent, in the dark, for 2 days to allow for disease development and were then returned to the glasshouse. After a further 3 days the level of disease development on each leaf was rated using a scale of 0-3.

A series of plants of the same age (4 replicates) which were untreated (i.e. not sprayed) were subjected to inoculation and assessment and used for comparison as untreated samples.

Results

Average infection rating for each leaf level on the replicates are shown in Figure 14. Infection on the leaves treated with the copper/zinc combination product is less than that found for other treatments.

Example 10 - The use of a combined copper silicate/zinc silicate composition and copper/zinc non-silicate combination for preventing *Botrytis* infection by spray application

Materials and Method

Healthy tomato seedlings (var. Gross Lisse) approximately 25-30cm in height were selected for use in the experiment. Treatments used were:

a) CZC #1: Copper/zinc silicate solution (0.56g/L as copper and 0.56g/L as zinc)

b) CZC #2: Copper/zinc silicate solution (0.28g/L as copper and 0.28g/L as zinc)

c) CZC #3: Copper/zinc silicate solution (0.14g/L as copper and 0.14g/L as zinc)

d) Kocide 20/20 #1 Suspension: (0.56g/L as copper and 0.56g/L as zinc)

e) Kocide 20/20 #2 Suspension (0.28g/L as copper and 0.28g/L as zinc)

f) Kocide 20/20 #2 Suspension (0.14g/L as copper and 0.14g/L as zinc)

Four plants were used as replicates for each treatment. Plants were sprayed with treatments and then, 3 days after the initial spray application the plants were inoculated with a spore suspension of *Botrytis cinerea*. After inoculation, the plants were contained in a humid infection tent, in the dark, for 2 days to allow for disease development and were then returned to the glasshouse. After a further 3 days the level of disease development on each leaf was rated using a scale of 0-3.

A series of plants of the same age (4 replicates) which were untreated (i.e. not sprayed) were subjected to inoculation and assessment and used for comparison as untreated samples.

<u>Results</u>

Average infection ratings (for all leaves of all the replicates) are shown in Figure 15. Infection on the leaves treated with the silicate based combination product is less than that found for other treatments.

Example 11A – Field application of copper silicate and copper/zinc silicate to grapes

<u>Materials and Methods</u>

A field trial was conducted on grapevines using 9 applications of foliar sprays over a period of 5 months. The applications commenced when the shoots were 10-50cm long and were conducted on a regular basis over the trial period (day 0, 10, 20, 31, 43, 56, 73, 94 and 137). Details of the trial conditions are as follows:

Location:	Pokolbin, N.S.W.
Crop:	Wine grapes
Variety	Shiraz
Plot size	19.8 square meters
Treatment area:	4 individual vines (1 row by 1 panel)
Replication:	3
Randomized design	

Products used in the trial included: (i) CSH - Copper silicate solution and (ii) CZS5050H -Copper/zinc silicate solution. Two untreated sets of replicate plots were also included in the trial.

Various concentrations of each product were used for treatment as shown in the table below.

Treatment	[Cu] (g/L)	[Zn] (g/L)
Untreated A	0	0
Untreated B	0	0
CSH #1	1.40	0
CSH #2	0.70	0
CSH #3	0.35	0
CZS5050H #1	0.70	0.70
CZS5050H #2	0.35	0.35
CZS5050H #3	0.18	0.18

Treatments were applied as high volume to the point of run-off sprays using a motorised pump, hose and handgun. Individual concentrations were made up fresh for each application by dilution of the stock solution provided.

Phytotoxicity was assessed at several points during the trial with data from the last point (after final application and the greatest impact) shown here.

Whole plot phytotoxicity ratings were conducted using a 0 to 10 arithmetic rating scale where 0=no visible phytotoxicity and 10=100% effect (necrosis). Leaf phytotoxicity ratings were conducted by assessing the percentage of each leaf affected on 50 leaves per plot. In addition, the percent of leaves affected in each plot was also determined.

<u>Results</u>

Results are shown in Figure 16 and Tables 11.1 – 11.2 Solutions of copper/zinc silicate combinations show significantly less phytotoxicity than the use of copper silicate alone. Even when formulations containing the same concentration of copper are compared, significantly less impact is found in those formulations where copper and zinc together are present.

Table 11.1 - Phytotoxic impact in terms of average rating of percent of leaves (from 50 leaves in each plot assessed) showing some necrosis.

Treatment	Average Percent of Leaves with Necrosis
Untreated A	7.3
Untreated B	7.3
CSH #1	62.0
CSH #2	43.3
CSH #3	19.3
CZS5050H #1	18.7
CZS5050H #2	13.3
CZS5050H #3	10.0

Table 11.2 - Phytotoxic impact in terms of average rating of percent of leaf area (from 50 leaves in each plot assessed) showing some necrosis.

Treatment	Average Percent of Leaf area with Necrosis
Untreated A	0.2
Untreated B	0.1
CSH #1	9.6
CSH #2	4.1
CSH #3	1.0
CZS5050H #1	0.7
CZS5050H #2	0.5
CZS5050H #3	0.3

Example 11B - Field application of copper silicate and copper/zinc silicate to potatoes

Materials and Methods

A field trial was conducted on a potato crop using 6 applications of foliar sprays over a period of 2 months. The applications commenced approximately 2 weeks prior to flowering and were conducted on a regular basis over the trial period (day 0, 11, 20, 30, 39, 52). Details of the trial conditions are as follows:

Location	Mollingghip near Ballarat, Vic
Crop:	Potatoes
Variety:	Russett Burbank
Treatment area:	2.25 metres (3 rows) x 8 metres
Replication:	3
Randomised Block Design	

Products used in the trial included:

CSH Copper silicate solution

CZS5050H Copper/zinc silicate solution

Three untreated sets of replicate plots were also included in the trial. Various concentrations of each product were used for treatment as shown in the table hereunder.

Treatment	[Cu] (g/L)	[Zn] (g/L)
Untreated A	0	0
Untreated B	0	0
CSH #1	1.40	0
CSH #2	0.70	0
CSH #3	0.35	0
CZS5050H #1	0.70	0.70
CZS5050H #2	0.35	0.35
CZS5050H #3	0.18	0.18

Treatments were applied as high volume to the point of run-off sprays using a motorised pump, hose and handgun. Individual concentrations were made up fresh for each application by dilution of the stock solutions provided.

Phytotoxicity was assessed at several points during the trial with data from the last point (immediately prior to final application and the greatest impact) shown here.

Leaf phytotoxicity ratings were conducted by assessing the percentage of each leaves affected from 50 leaves per plot assessed. In addition, the mean phytotoxicity rating per leaf was calculated from individual leaf ratings of the 50 leaves per plot. Ratings used a scale of 0-5 where 0 = no impact and 5 = total leaf necrosis.

Results

Results are shown in Figures 17 and 18 and tables 11.3 and 11.4 Solutions of copper/zinc silicate combinations show significantly less phytotoxicity than the use

of copper silicate alone. Even when formulations containing the same concentration of copper are compared, significantly less impact is found in those formulations where copper and zinc together are present.

Table 11.3 - Phytotoxic impact in terms of average percent of leaves impacted per plot (from 50 leaves assessed per plot).

Treatment	**Average Percent of Leaves with Necrosis**
Untreated #1	0.0
Untreated #2	0.0
Untreated #3	0.0
CSH #1	100.0
CSH #2	100.0
CSH #3	53.3
CZS5050H #1	13.3
CZS5050H #2	4.0
CZS5050H #3	4.0

Table 11.4 - Phytotoxic impact in terms of mean phytotoxicity rating per leaf (from 50 leaves in each plot assessed). Scale [0-5].

Treatment	**Mean Phytotoxicity Rating per leaf**
Untreated #1	0
Untreated #2	0
Untreated #3	0
CSH #1	3.03
CSH #2	2.21
CSH #3	1.00
CZS5050H #1	0.16
CZS5050H #2	0.05
CZS5050H #3	0.05

Example 11C - Phytotoxic impact of copper silicate and copper/zinc silicate on various plant species.

Materials and Method

Healthy Petunia, Broccoli and Tomato seedlings were obtained from commercial nurseries and potted into individual 14 cm pots. After growing under glasshouse conditions for approximately 2 weeks the seedlings were sprayed with individual

treatments as outlined below. Application used hand held trigger spray applicators with each plant sprayed just prior to the point of run-off.

Products used were: (i) CZC – Copper/zinc silicate solution (ii) CSH – Copper silicate solution and (iii) ZSH – Zinc silicate solution.

A variety of concentrations were used for each product. Treatments used are listed in the table hereunder together with the various concentrations used.

Treatment	[Cu] (g/L)	[Zn] (g/L)
Untreated	0	0
CZC #1	0.56	0.56
CZC #2	0.28	0.28
CZC #3	0.14	0.14
CSH #1	1.12	0
CSH #2	0.56	0
CSH #3	0.28	0
ZSH #1	0	1.12
ZSH #2	0	0.56
ZSH #3	0	0.28

Three plants were used as replicates for each treatment. Plants were sprayed with treatments and then, 4 days after the initial spray application the plants were assessed for phytotoxic effects. Individual plants were rated for necrosis on a scale of 0-5 where 0 = no damage and 5 = all leaves and foliage showing damage.

Results

Results are shown in Table 11.5. Solutions of copper/zinc silicate combinations show significantly less phytotoxic impact than the use of copper silicate alone. Even when formulations containing the same concentration of copper are compared, significantly less impact is found in those formulations where copper and zinc together are present. The use of zinc silicate alone has little or no impact.

Table 11.5 - Average rating of phytotoxic damage resulting on plants after various treatments. Rating scale (0-5).

Treatment	Damage rating (0-5) after 4 days		
	Petunia	Broccoli	Tomato
Untreated	0.0	0.0	0.0
CZC #1	0.0	0.0	0.5
CZC #2	0.3	0.0	0.0
CZC #3	0.6	0.0	0.0
CSH #1	4.2	3.5	2.2
CSH #2	3.2	1.0	1.2
CSH #3	2.0	0.3	0.2
ZSH #1	0.3	0.0	0.0
ZSH #2	0.0	0.2	0.0
ZSH #3	0.0	0.0	0.0

Example 12 – Systemic activity of copper silicate and zinc silicate compositions when applied to parts of mature plants.

<u>General Material and Methods</u>

Tomato plants (*var. Grosse Lisse*) were partially sprayed with fungicide solutions by placing a cardboard barrier over each individual plant such that only half the leaves (on one side of the plant) were sprayed. The barrier prevented any spray drift from contacting the "untreated" side of each plant.

After 5 days under glasshouse conditions plants were then inoculated with a suspension of Botrytis cinerea spores and transferred into an "infection tent" (an enclosed, high humidity environment) for 48 hours. After this time, the plants were transferred back to the glasshouse and maintained for a further 5 days. At this point (12 days after the initial application of product and 7 days after inoculation) the leaves of each plant were individually rated for disease development using a standard half integer scale of 0-3 (see Figure 1).

Within the time period between application and disease rating (12 days) each plant grew substantially adding a number of leaves (4-6). As a result, each plant could be categorised into three individual parts:

- The base area of the plant that was sprayed with fungicide
- The base area of the plant that was NOT sprayed with fungicide
- The new growth area of the plant that was NOT sprayed with fungicide

Ratings of disease development on the leaves in each category were combined for individual plants and the results from replicate plants (5) of the same treatment were then averaged. The result gives a disease development rating for each individual category of plant treatment for each of the applications used.

Example 12A

Application No.	Treatment
1	Untreated
2	CS100 - Copper silicate (1.12g/L as Cu)
3	CZS5050 - Copper/zinc silicate (0.56g/L Cu, 0.56g/L Zn)
4	Kocide (1g/L as Cu)
5	S100 - Sodium Silicate solution (equiv. to 3 & 4)

Results

These are shown in Table 12.1.

Table 12.1 Average disease rating of plant areas across replicates.

Treatment	Base Sprayed	Base Unsprayed	Tip Unsprayed
Untreated	1.53	1.58	0.75
CS100	1.13	1.08	0.40
CZS5050	1.16	1.10	0.39
Kocide	1.16	1.47	0.67
S100	1.51	1.30	0.69

Example 12B.

Application No.	Treatment
1	Untreated
2	CS100 - Copper silicate (1.12g/L as Cu)
3	ZS100 - Zinc silicate (1.12g/L as Zn)
4	Kocide (1g/L as Cu)

Results

These are shown in Table 12.2.

Table 12.2 Average disease rating of plant areas across replicates.

Treatment	Base Sprayed	Base Unsprayed	Tip Unsprayed
Untreated	1.44	1.36	0.47
CS100	0.83	0.87	0.23
ZS100	0.94	0.95	0.25
Kocide	0.35	1.16	0.43

Example 12C.

Application No.	Treatment
1	Untreated
2	CS100 - Copper silicate (1.12g/L as Cu)
3	CZS5050 – Copper/Zinc silicate (0.56g/L Cu, 0.56g/L Zn)
4	S100 - Sodium Silicate solution (equiv. to 2 & 3)

Results

These are shown in Table 12.3.

Table 12.3. Average disease rating of plant areas across replicates.

Treatment	Base Sprayed	Base Unsprayed	Tip Unsprayed
Untreated	2.19	2.13	1.04
CS100	1.30	1.29	0.52

CZS5050	1.29	1.41	0.54
S100	1.71	1.76	0.97

Example 13: Systemic activity of copper silicate and zinc silicate compositions when applied to growing plants

General Materials and Methods

Tomato plants (*var. Grosse Lisse*) were sprayed with fungicide solutions (replication = 4 per treatment). After 23 days under glasshouse conditions plants were then inoculated with a suspension of Botrytis cinerea spores and transferred into an "infection tent" (an enclosed, high humidity environment) for 36 hours. After this time, the plants were transferred back to the glasshouse and maintained for a further 5 days. At this point the leaves of each plant were individually rated for disease development using a standard half integer scale of 0-3 (see attached.)

Over the course of the experiment the plants grew substantially such that the top half of the plants at inoculation were essentially new growth post the application of the fungicide solutions. As a result, assessment of disease development on the top half of plants (tip-L6) in each case gives an indication of any systemic activity of the products.

This test was repeated 4 times using the same design. The results of each test are shown below in Examples 13A-F.

Example 13A

Application No.	**Treatment**
1.	Untreated
2	Kocide (1g/L as Cu)
3	CS100 - Copper silicate (1.12g/L as Cu)
4	ZS100 – Zinc silicate (1.12g/L as Zn)
5	CZS5050 – Copper/Zinc silicate (0.56g/L Cu, 0.56g/L Zn)

Results

These are set out in Table 13.1

Table 13.1 - Average disease rating of plant areas across replicates.

Treatment	Average Disease Rating of Tip-L6
Untreated	1.06
Kocide	0.98
CS100	0.44
ZS100	0.41
CZS5050	0.39

Example 13B

Application No.	Treatment
1	Untreated
2	Kocide (1g/L as Cu)
3	CS100 - Copper silicate (1.12g/L as Cu)
4	ZS100 – Zinc silicate (1.12g/L as Zn)
5	CZS5050 – Copper/Zinc silicate (0.56g/L Cu, 0.56g/L Zn)

Results

These are set out in Table 13.2

Table 13.2 - Average disease rating of plant areas across replicates.

Treatment	Average Disease Rating of Tip-L6
Untreated	1.11
Kocide	1.18

CS100	0.93
ZS100	0.95
CZS5050	0.91

Example 13C

Application No.	Treatment
1	Untreated
2	Kocide (1g/L as Cu)
3	CS100 - Copper silicate (1.12g/L as Cu)
4	ZS100 – Zinc silicate (1.12g/L as Zn)
5	CZS5050 – Copper/Zinc silicate (0.56g/L Cu, 0.56g/L Zn)

Results

These are set out in Table 13.3.

Table 13.3 - Average disease rating of plant areas across replicates.

Treatment	Average Disease Rating of Tip-L6
Untreated	0.72
Kocide	0.63
CS100	0.39
ZS100	0.41
CZS5050	0.30

Example 13D

Application No.	Treatment
1	Untreated
2	Kocide (1g/L as Cu)
3	CS100 - Copper silicate (1.12g/L as Cu)
4	ZS100 – Zinc silicate (1.12g/L as Zn)
5	CZS5050 – Copper/Zinc silicate (0.56g/L Cu, 0.56g/L Zn)

Results

These are set out in Table 13.4.

Table 13.4 - Average disease rating of plant areas across replicates.

Treatment	Average Disease Rating of Tip-L6
Untreated	1.02
Kocide	0.73
CS100	0.52
ZS100	0.63
CZS5050	0.18

Example 13E

In this example a range of concentrations of the copper/zinc silicate product were assessed.

Application No.	Treatment
1	1 Untreated
2	2 S100 – Sodium silicate solution
3	3 CZS5050 – Copper/Zinc silicate (0.56g/L Cu, 0.56g/L Zn)
4	4 CZS5050 – Copper/Zinc silicate (0.28g/L Cu, 0.28g/L Zn)
5	5 CZS5050 – Copper/Zinc silicate (0.14g/L Cu, 0.14g/L Zn)

Results

These are set out in Table 13.5.

Table 13.5 - Average disease rating of plant areas across replicates.

Treatment	Average Disease Rating of Tip-L6
Untreated	1.69
S100	2.08

CZS5050	1.28
CZS5050	1.75
CZS5050	1.21

Example 13F

Application No.	Treatment
1	Untreated
2	S100 – Sodium silicate solution
3	CZS5050 – Copper/Zinc silicate (0.56g/L Cu, 0.56g/L Zn)
4	CZS5050 – Copper/Zinc silicate (0.28g/L Cu, 0.28g/L Zn)
5	CZS5050 – Copper/Zinc silicate (0.14g/L Cu, 0.14g/L Zn)

Results

These are set out in Table 13.6.

Table 13.6 - Average disease rating of plant areas across replicates.

Treatment	Average Disease Rating of Tip-L6
Untreated	1.44
S100	1.43
CZS5050	1.20
CZS5050	1.18
CZS5050	1.37

Other modifications and adaptations apparent to one skilled in the art are encompassed by the present invention.

The Claims Defining the Invention are as Follows

1 A method for controlling microbes comprising the step of contacting said microbes with an effective amount of copper silicate and zinc silicate.

2 A method according to claim 1 wherein the microbes are bacteria and/or fungi.

3 A method according to claim 1 or 2 wherein the copper silicate and zinc silicate are applied to a plant infected with the microbes.

4 A method according to claim 3 wherein the plant is a crop.

5 A method according to claim 3 wherein the plant is at least one domestic plant.

6 A method for preventing microbial growth comprising the step of administering to an environment with a potential to contain the microbes an effective amount of copper silicate and zinc silicate.

7 A method according to any one of the preceding claims wherein the microbes are plant pathogens.

8 A method according to claim 7 wherein the plant pathogen is at least one microbe selected from the group comprising *Botrytis. spp* such as, *B. squamosa*, *B. tulipae*, *B fabae* and *B cinerea; Legionella spp; Aschocyts spp such as A rabiei* and *A lentis; Altenaria spp* such as *Altenaria altenata; and Colleotrichum spp* such as *C gloeosporoides*.

9 A method according to claim 1 wherein the microbes are controlled by at least inhibiting their growth and/or totally preventing their growth.

10 A method according to claim 1 wherein the copper silicate and zinc silicate are applied as separate components.

11 A method according to claim 10 wherein the silicates are applied sequentially or simultaneously.

12 A method according to claim 1 wherein the copper silicate and zinc silicate are applied as a single mixture.

13 A method according to claim 1 wherein the copper silicate is an aqueous solution of acidified copper silicate.

14 A method according to claim 1 wherein the effective amount of copper silicate is a final concentration of approximately 0.04 g/L - 1.4g/L, 0.1 g/L – 1 g/L or 0.3 to 0.8 g/L (as Cu).

15 A method according to claim 14 wherein the effective amount of copper silicate is to a final concentration of approximately 0.56 g/L (as Cu).

16 A method according to claim 1 wherein the zinc silicate is an aqueous solution of acidified zinc silicate.

17 A method according to claim 1 wherein the effective amount of zinc silicate is to a final concentration of approximately 0.04 g/L - 1.4g/L, 0.1 g/L – 1 g/L or 0.3 to 0.8 g/L (as Zn).

18 A method according to claim 17 wherein the effective amount of zinc silicate is to a final concentration of approximately 0.56 g/L (as Zn).

19 A method according to claim 1 wherein the ratio of copper (final concentration) to zinc (final concentration) is between approximately 40:1 and 1:40.

20 A method according to claim 19 wherein the ratio of copper (final concentration) to zinc (final concentration) is 1:20 or 20:1, 1:10 or 10:1, 1:4 or 4:1, 1:3 or 3:1.

21 A method according to claim 1 wherein the ratio of copper (final concentration) to zinc (final concentration) is 1:1.

22 A method according to claim one wherein multiple doses of the copper silicate and zinc silicate are applied.

23 A composition comprising copper silicate and zinc silicate in amounts effective to control microbes.

24 A composition according to claim 23 wherein the compositions comprise at least approximately 0.04 g/L - 1.4g/L, 0.1 g/L – 1 g/L or 0.3 to 0.8 g/L of both copper silicate (as Cu) and zinc silicate (as Zn).

25 A composition according to claim 23 wherein the composition comprises at least approximately 0.7-1.4g/L of both copper silicate (as Cu) and zinc silicate (as Zn).

26 A composition according to claim 23 wherein the composition comprises 0.56g/L copper silicate (as Cu) and zinc silicate (as Zn).

27 A composition according to claim 23 wherein the composition comprises a synergistic amount of copper silicate and zinc silicate.

28 A composition according to claim 23 wherein the ratio of copper silicate to zinc silicate in the compositions is selected from the group comprising approximately 1:1 or between 40:1 and 1:40 such as, 1:20 or 20:1, 1:10 or 10:1, 1:4 or 4:1, 1:3 or 3:1.

29 A composition according to claim 23 adapted for topical application.

30 A composition according to claim 29 adapted for spraying.

31 A method for treating a microbial infection comprising the step of: contacting a copper silicate and zinc silicate composition with the infection for sufficient time to substantially remove or control the infection.

32 A method of producing a copper silicate and zinc silicate composition, the method comprising the steps of:

(i) reacting a copper salt with an alkali silicate in an acidic solvent to produce an aqueous solution of acidified copper silicate;

(ii) reacting a zinc salt with an alkali silicate in an acidic solvent to produce an aqueous solution of acidified copper silicate; and

(iii) combining the products of (i) and (ii) to form the composition.

33 A method according to claim 32 wherein steps (i) and (ii) are carried out independently and then the respective products added together to form the composition.

34 A method of producing a copper silicate and zinc silicate composition, the method comprising the steps of:

(i) reacting a copper salt with an alkali silicate in an acidic solvent to produce an aqueous solution of acidified copper silicate; and

(ii) reacting a zinc salt with an alkali silicate in an acidic solvent to produce an aqueous solution of acidified copper silicate; wherein steps (i) and (ii) are carried out simultaneously in a single reaction vessel to form the composition.

35 A method of producing a copper silicate and zinc silicate composition, the method comprising the steps of:

(i) reacting a copper salt with an acidic solvent;

(ii) reacting a zinc salt with an acidic solvent; and

(iii) reacting the products from (i) and (ii) with an alkali silicate to form the composition.

36 A method according to any one of the claims 32 to 35 wherein the acidic solvent buffers the mixture of the salts and alkali silicate such that the acidified copper silicate and zinc silicate has a pH in the range of 2 to 6.

37 A method according to claim 36 wherein the pH is in a range of 3 to 5.

38 A method according to any one of claims 32 to 37 wherein the acidic solvent is a mixture of acetic acid and sodium acetate.

39 A method according to any one of claims 32 to 38 wherein the salts are sulphates, oxides, hydroxides or chlorides.

40 A method according to any one of claims 32 to 39 wherein the alkali silicate is sodium silicate.

41 A method according to any one of claims 32 to 40 further comprising the step of using water to dilute one or more of the reactants.

42 A composition made according to the method of any one of claims 32 to 41.

Figure 1

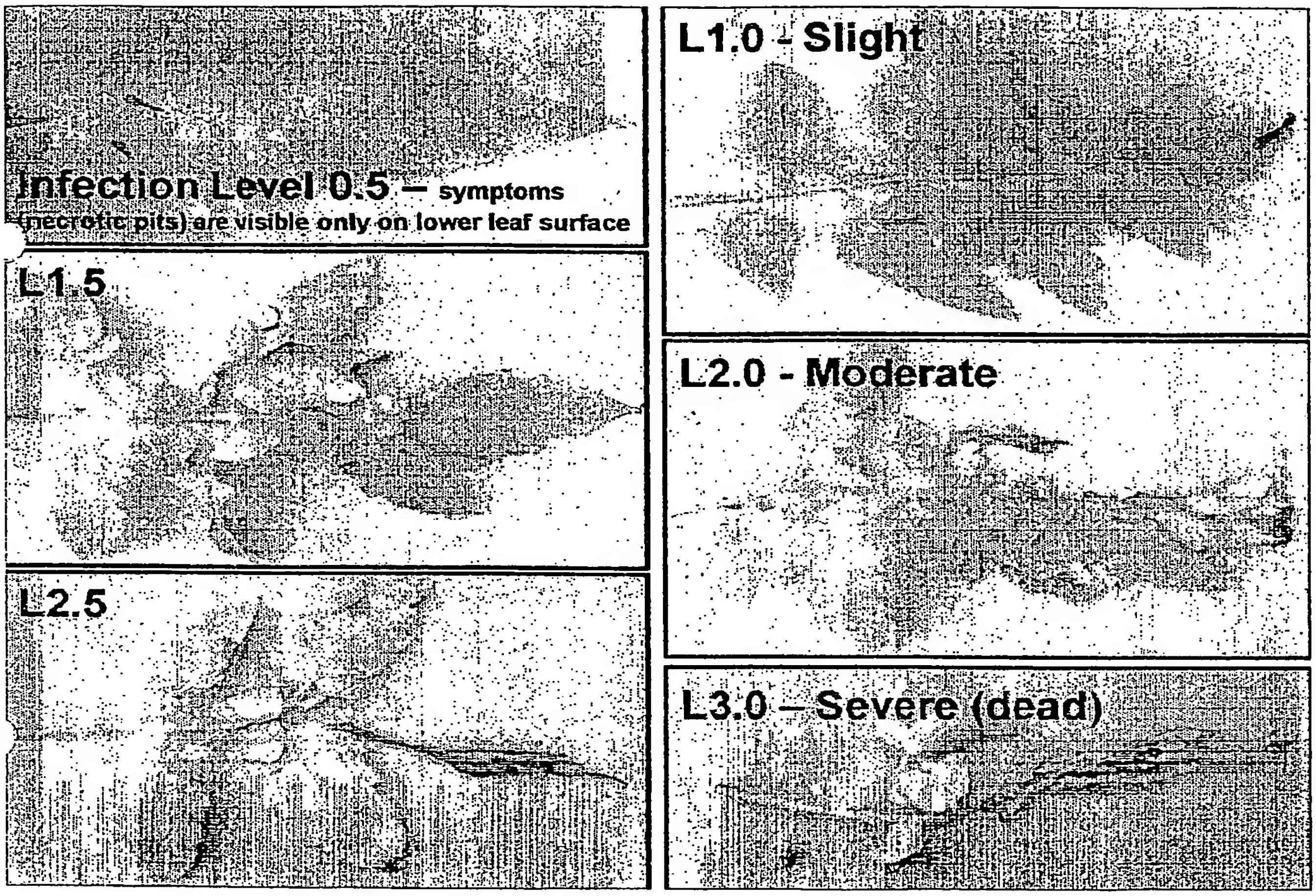

Infection Level 0.5 – symptoms (necrotic pits) are visible only on lower leaf surface
L1.0 - Slight
L1.5
L2.0 - Moderate
L2.5
L3.0 – Severe (dead)

Figure 2.

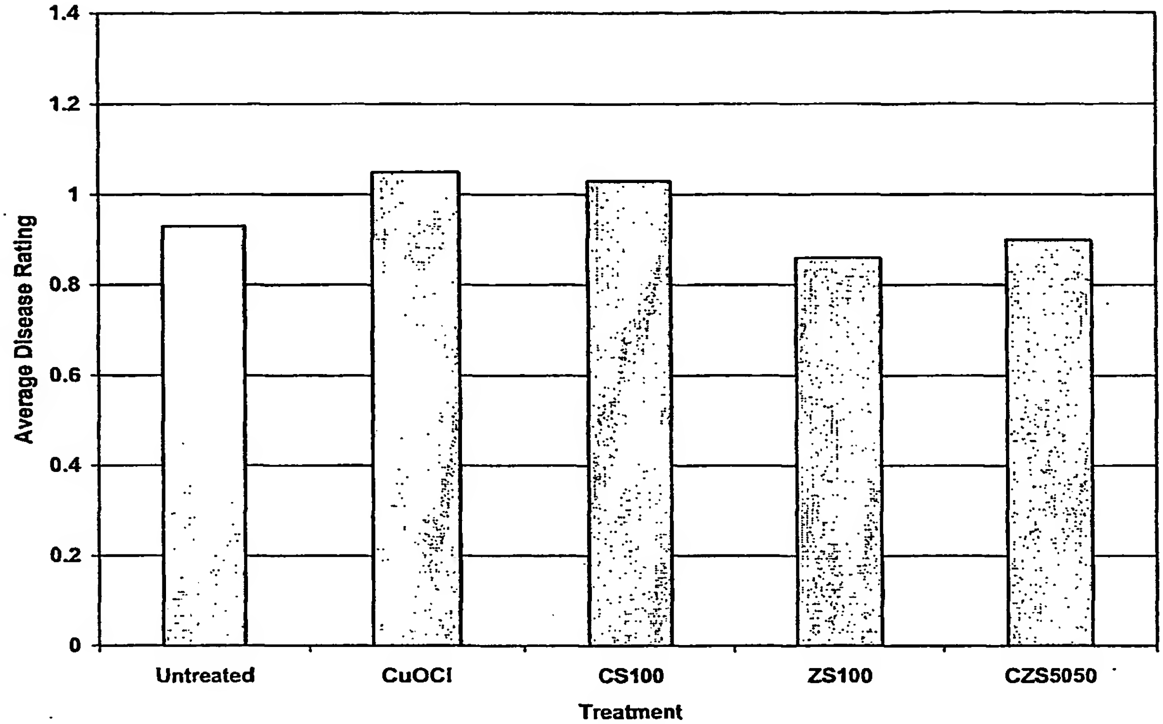

1.4
1.2
1
0.8
0.6
0.4
0.2
0
Average Disease Rating
Untreated
CuOCl
CS100
ZS100
CZS5050
Treatment

Figure 3.

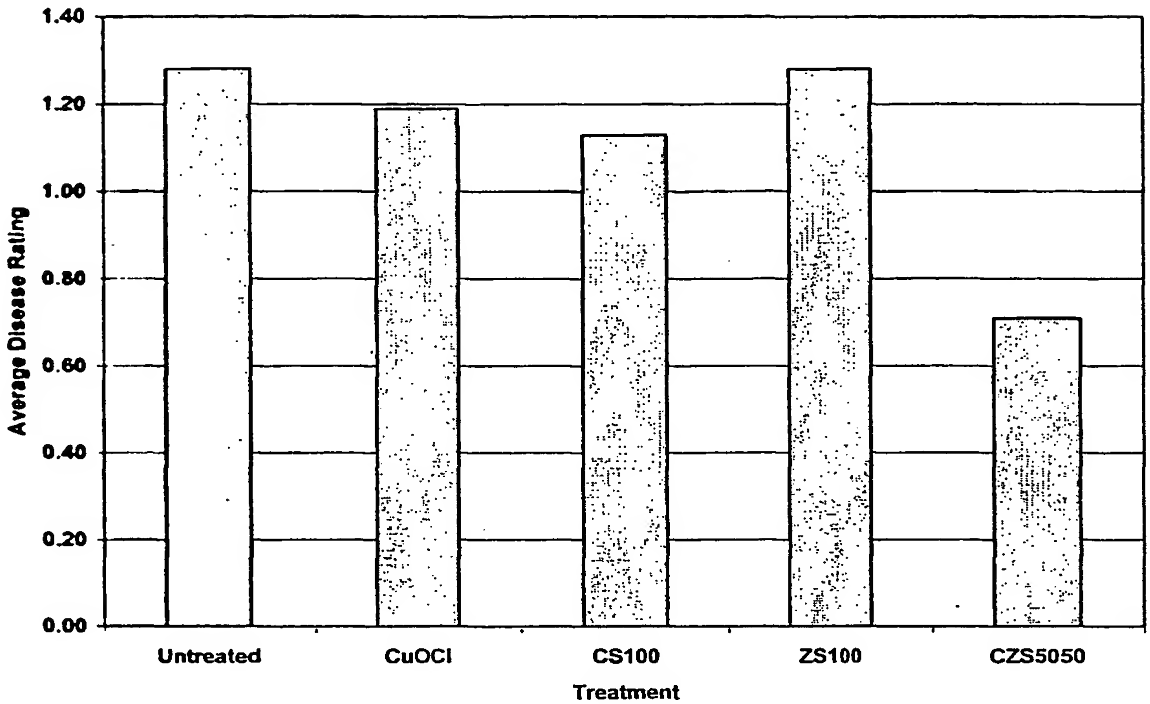

1.40
1.20
1.00
0.80
0.60
0.40
0.20
0.00
Average Disease Rating
Untreated
CuOCl
CS100
ZS100
CZS5050
Treatment

Figure 4.

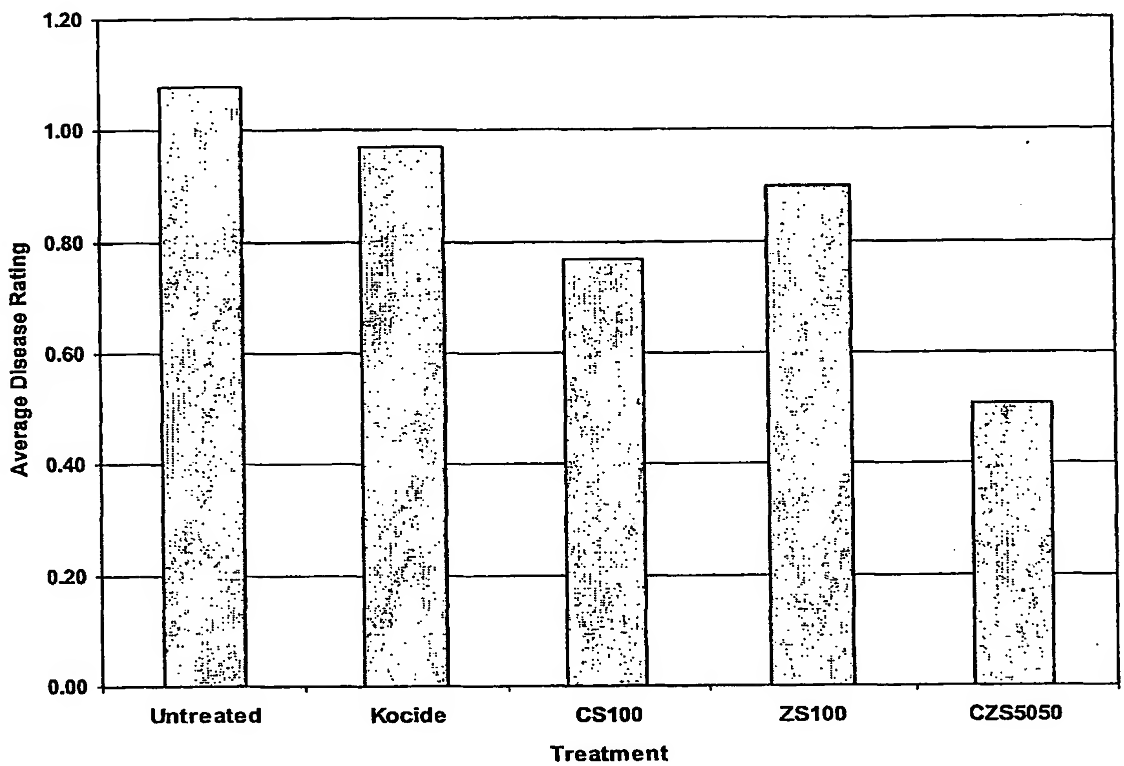

1.20
1.00
0.80
0.60
0.40
0.20
0.00
Average Disease Rating
Untreated
Kocide
CS100
ZS100
CZS5050
Treatment

Figure 5a.

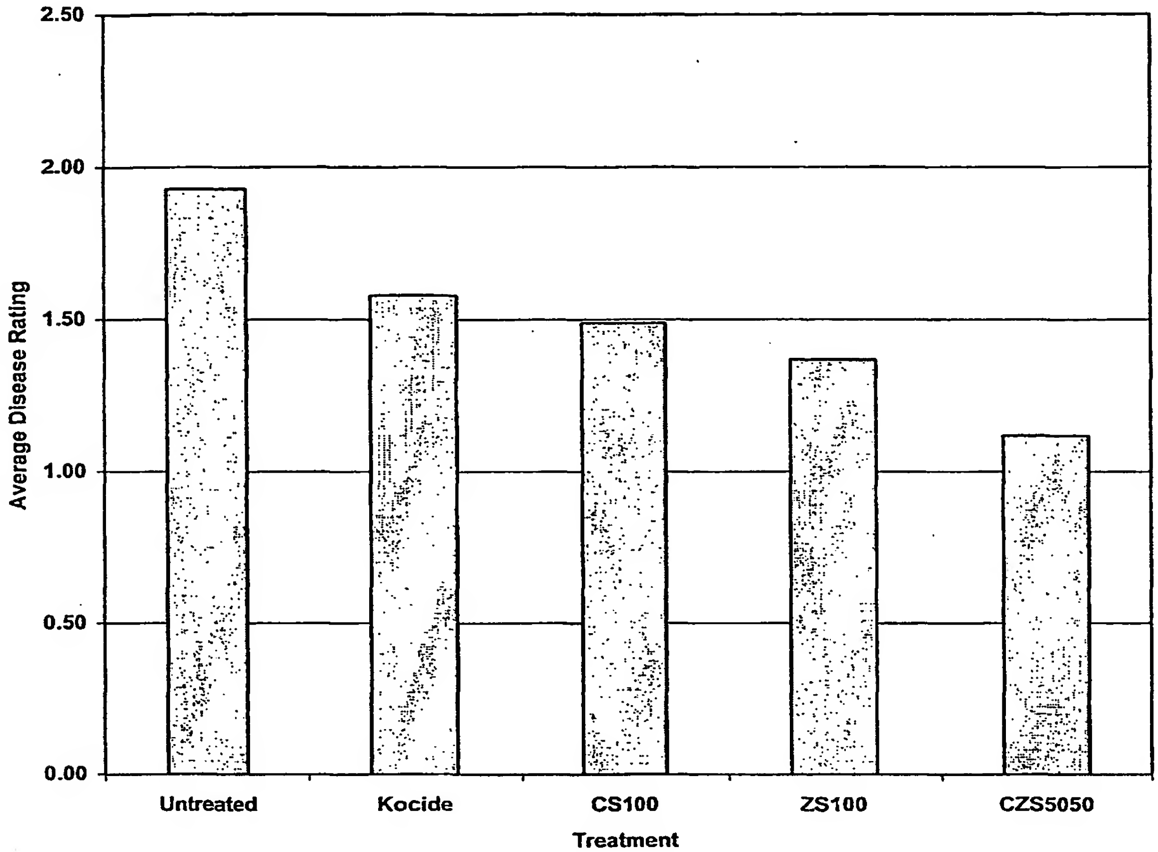

2.50
2.00
1.50
1.00
0.50
0.00
Average Disease Rating
Untreated
Kocide
CS100
ZS100
CZS5050
Treatment

Figure 5b.

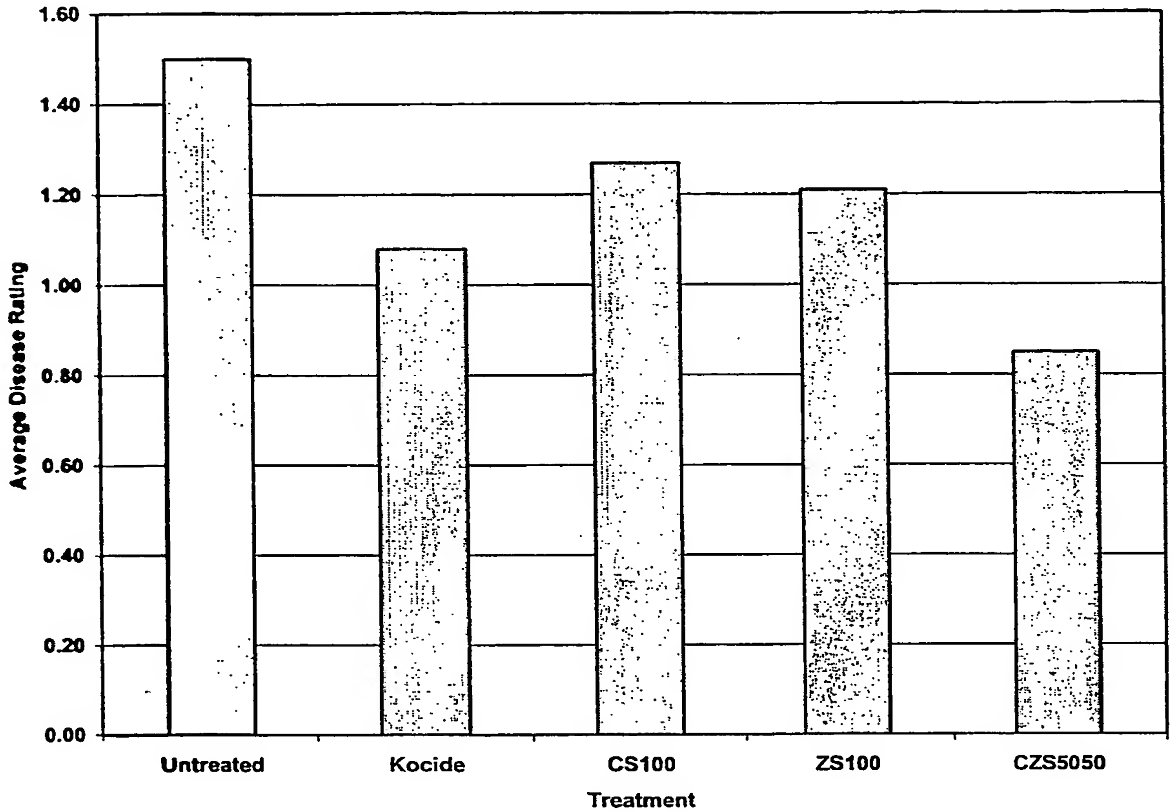

1.60
1.40
1.20
1.00
0.80
0.60
0.40
0.20
0.00
Average Disease Rating
Untreated
Kocide
CS100
ZS100
CZS5050
Treatment

Figure 6a.

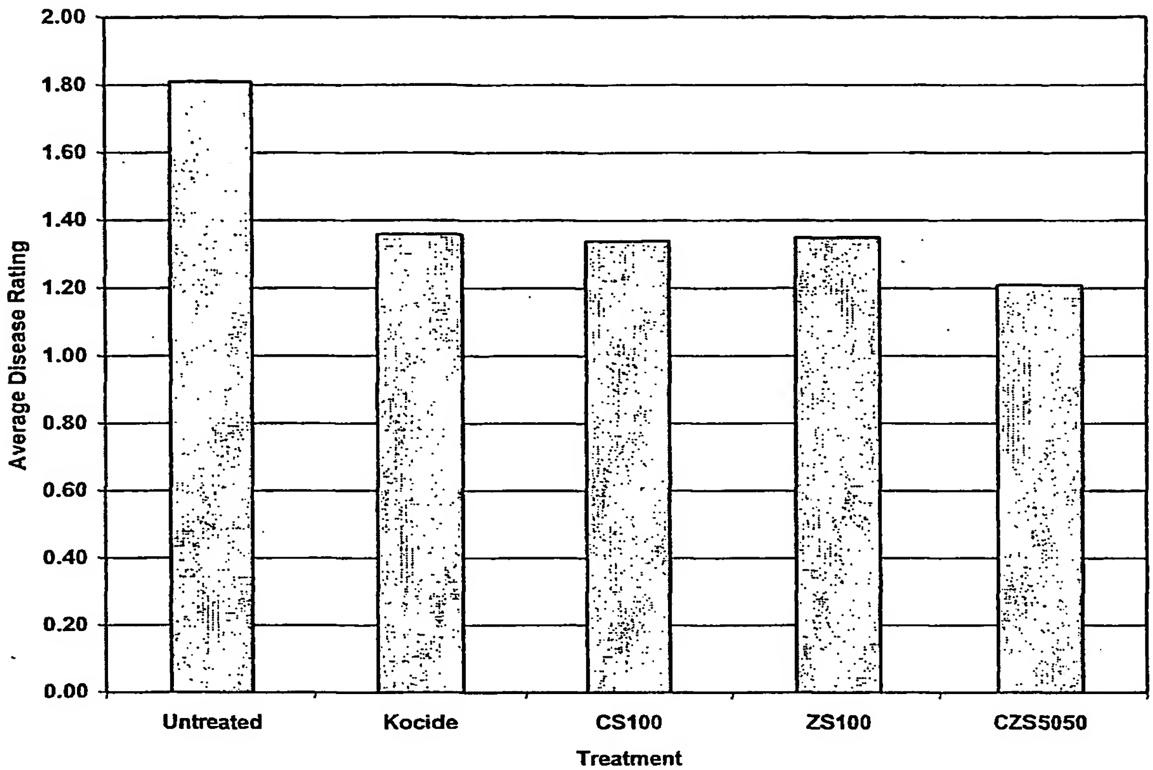

2.00
1.80
1.60
1.40
1.20
1.00
0.80
0.60
0.40
0.20
0.00
Average Disease Rating
Untreated
Kocide
CS100
ZS100
CZS5050
Treatment

Figure 6b.

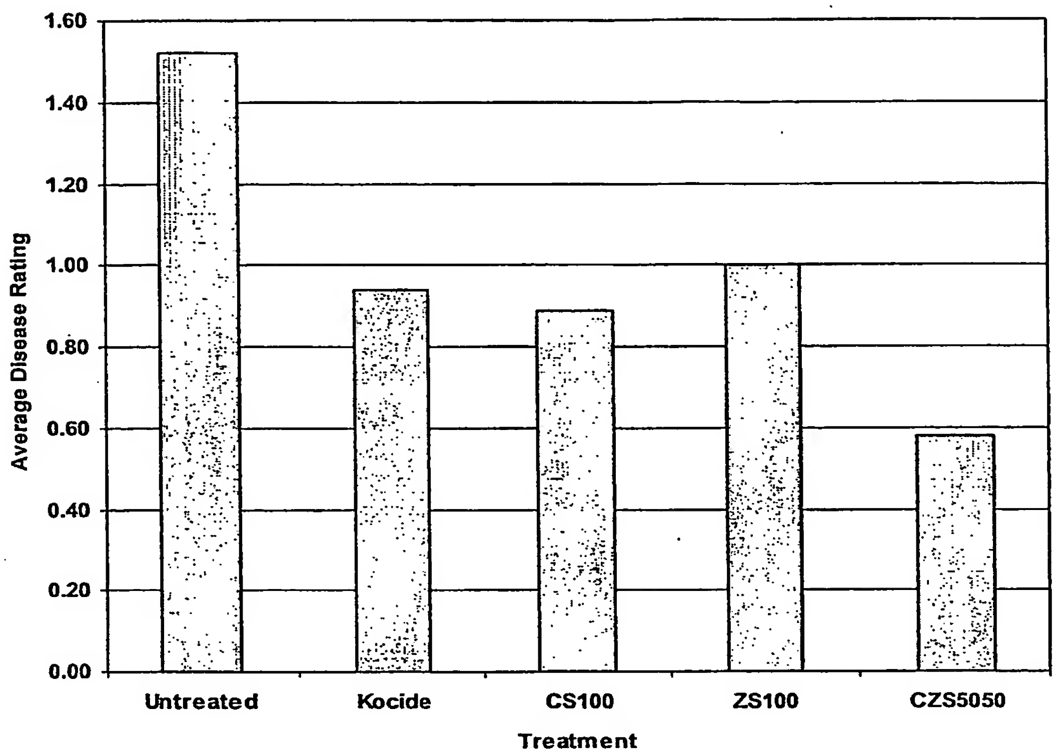

1.60
1.40
1.20
1.00
0.80
0.60
0.40
0.20
0.00
Average Disease Rating
Untreated
Kocide
CS100
ZS100
CZS5050
Treatment

Figure 7.

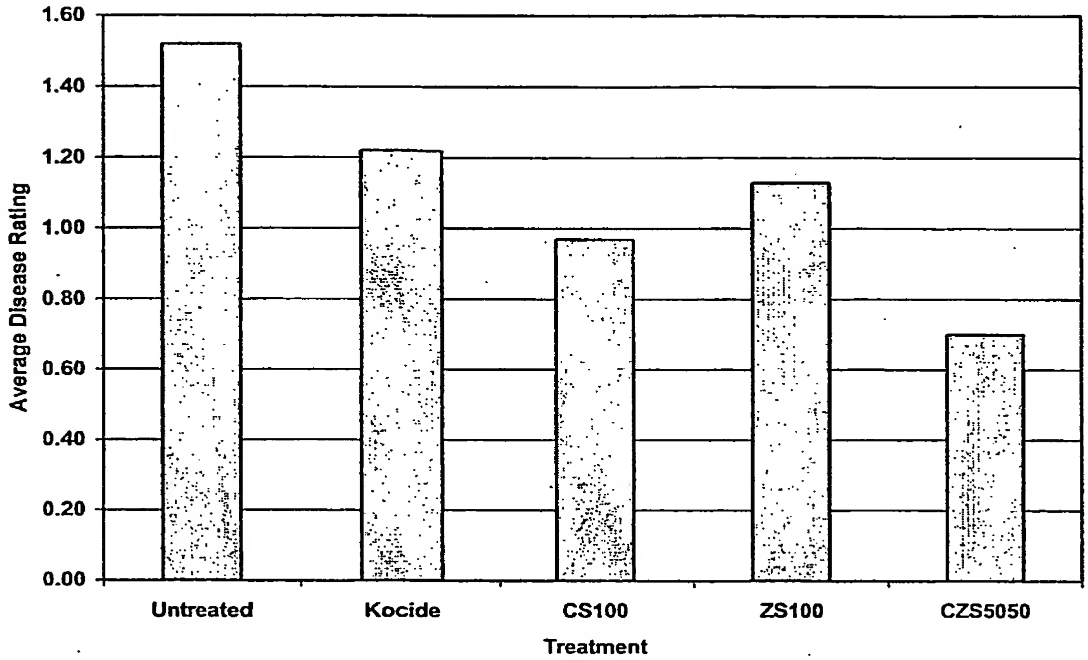

1.60
1.40
1.20
1.00
0.80
0.60
0.40
0.20
0.00
Average Disease Rating
Untreated
Kocide
CS100
ZS100
CZS5050
Treatment

Figure 8

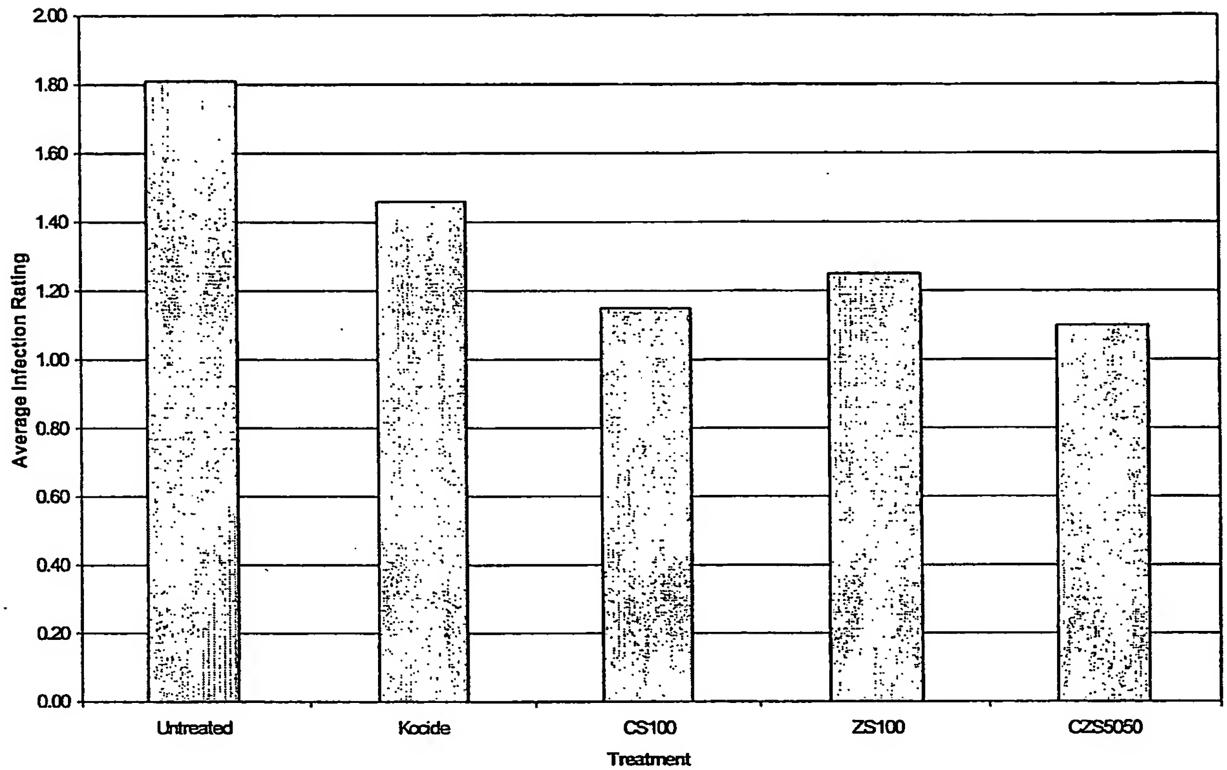

2.00
1.80
1.60
1.40
1.20
1.00
0.80
0.60
0.40
0.20
0.00
Average Infection Rating
Untreated
Kocide
CS100
ZS100
CZS5050
Treatment

Figure 9

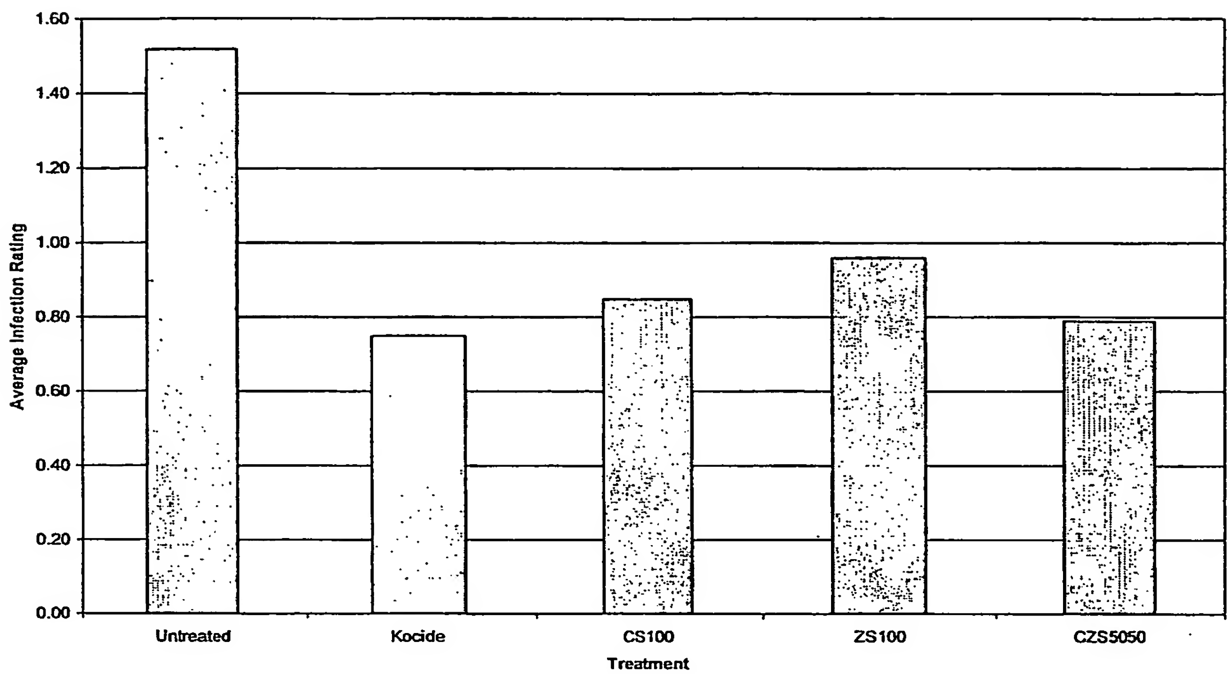

1.60
1.40
1.20
1.00
0.80
0.60
0.40
0.20
0.00
Average Infection Rating
Untreated
Kocide
CS100
ZS100
CZS5050
Treatment

Figure 10

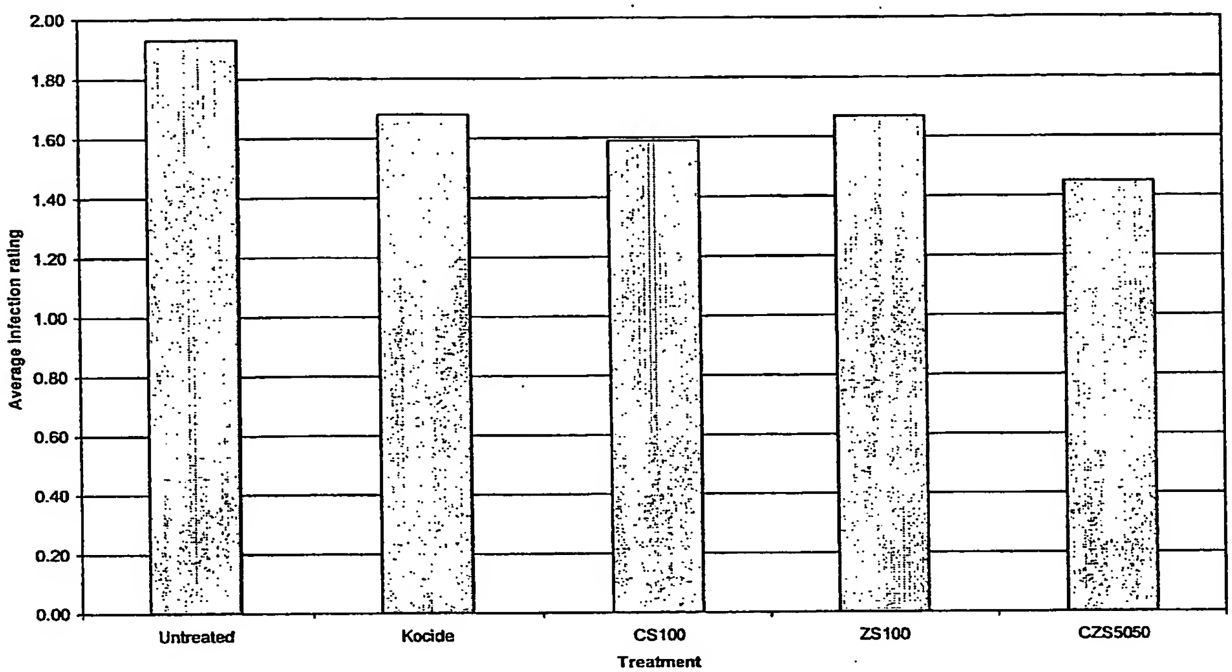

2.00
1.80
1.60
1.40
1.20
1.00
0.80
0.60
0.40
0.20
0.00
Average infection rating
Untreated
Kocide
CS100
ZS100
CZS5050
Treatment

Figure 11

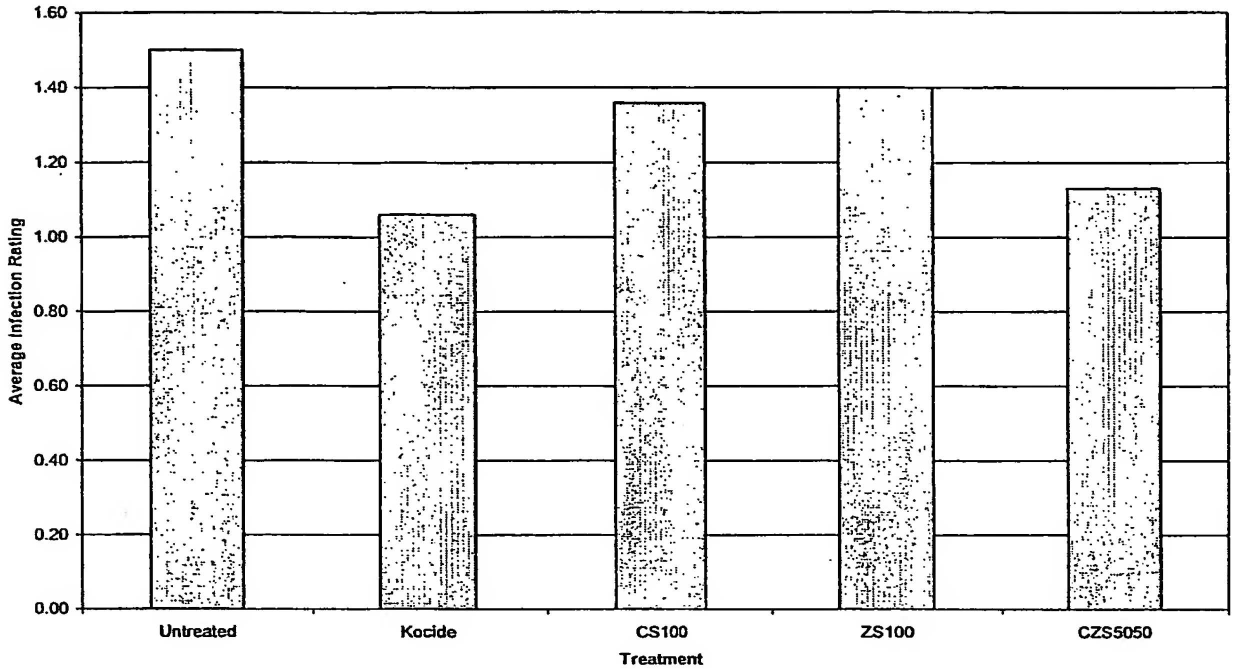
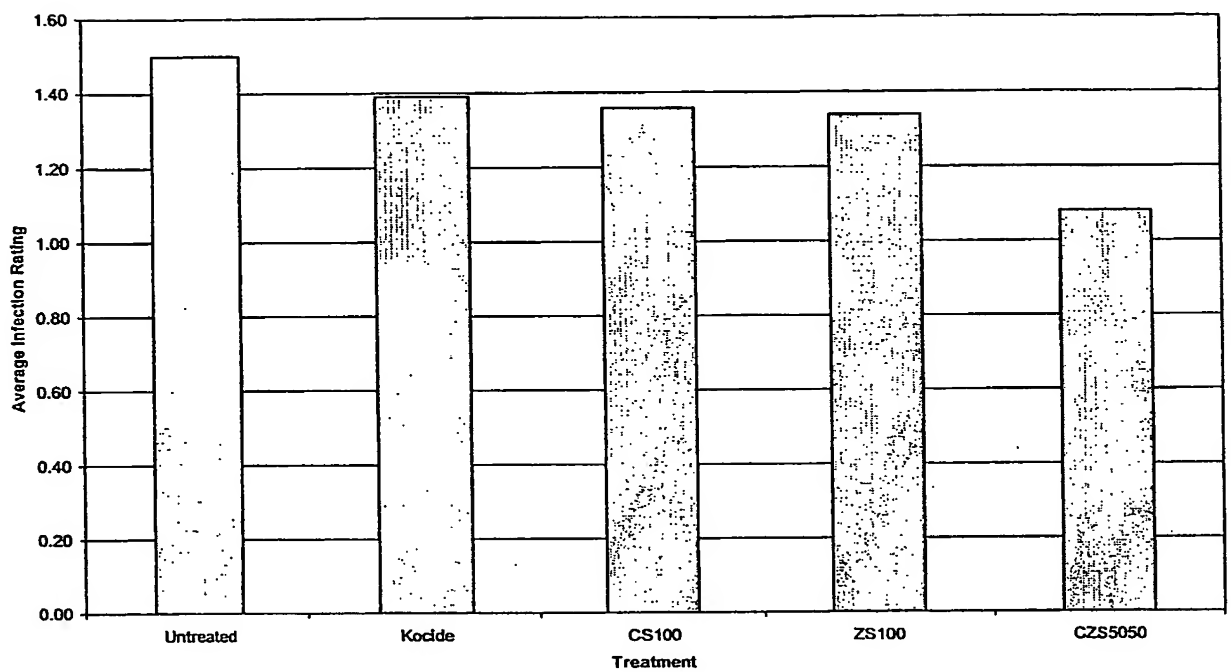
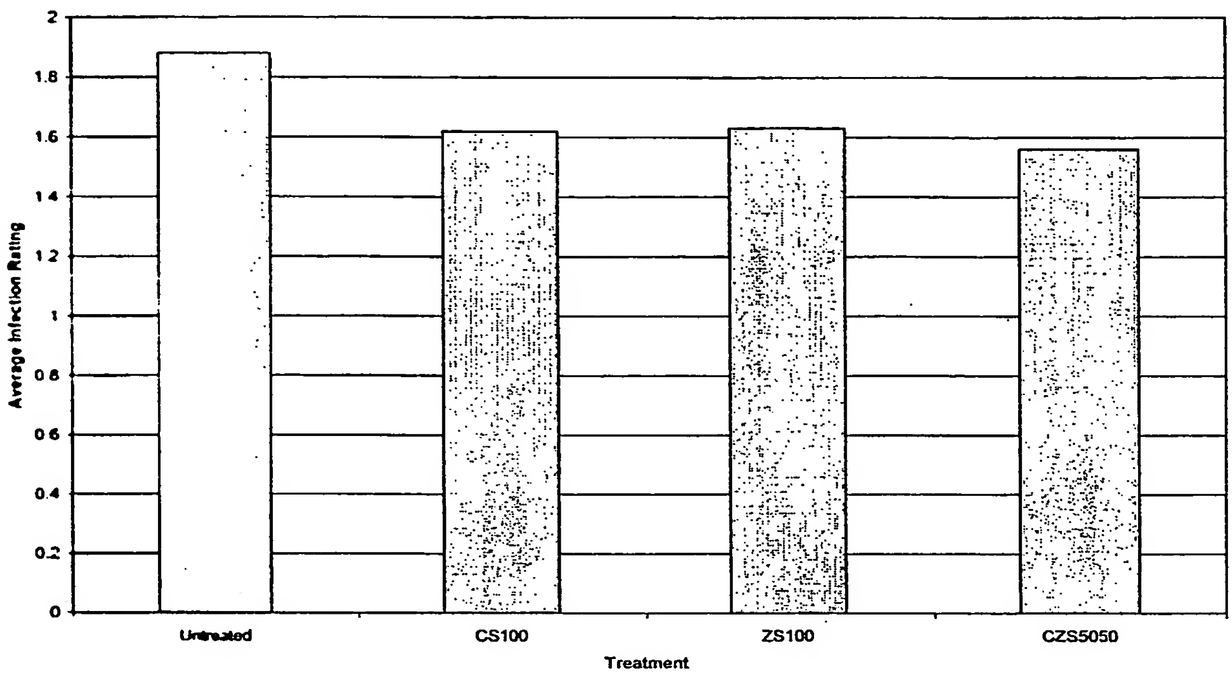

1.60
1.40
1.20
1.00
0.80
0.60
0.40
0.20
0.00
Average Infection Rating
Untreated
Kocide
CS100
ZS100
CZS5050
Treatment

Figure 12



1.60
1.40
1.20
1.00
0.80
0.60
0.40
0.20
0.00
Average Infection Rating
Untreated
Kocide
CS100
ZS100
CZS5050
Treatment

Figure 13



Average Infection Rating
2
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
Untreated
CS100
ZS100
CZS5050
Treatment

Figure 14

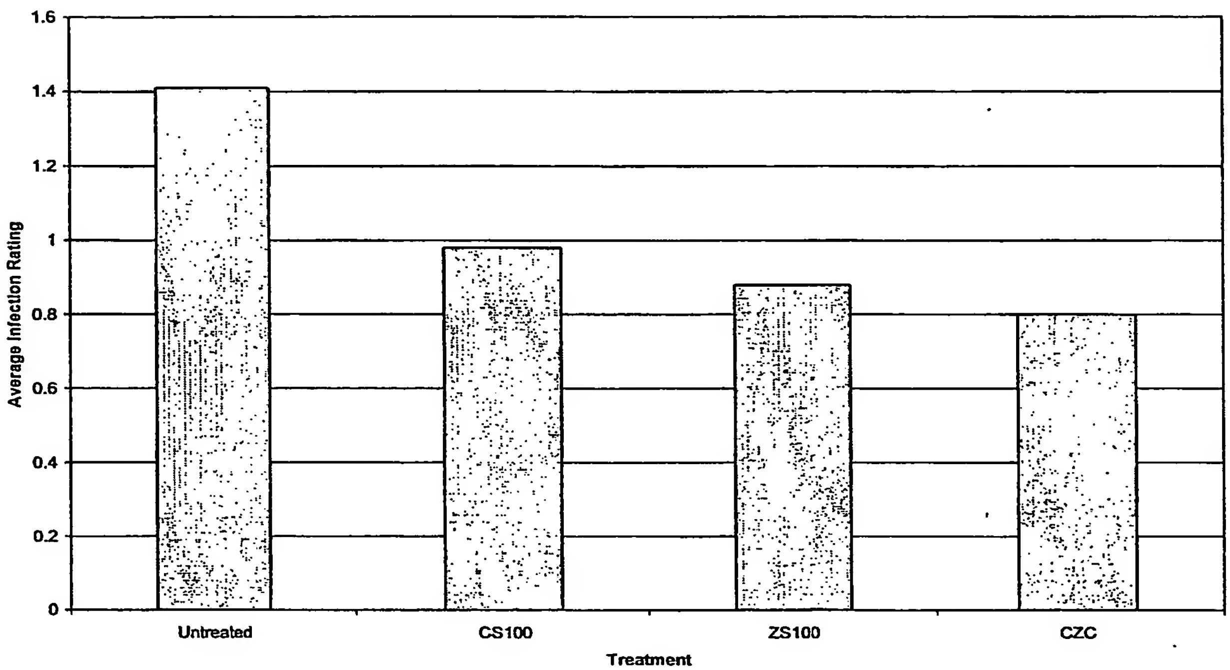

Average Infection Rating
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
Untreated
CS100
ZS100
CZC
Treatment

Figure 15

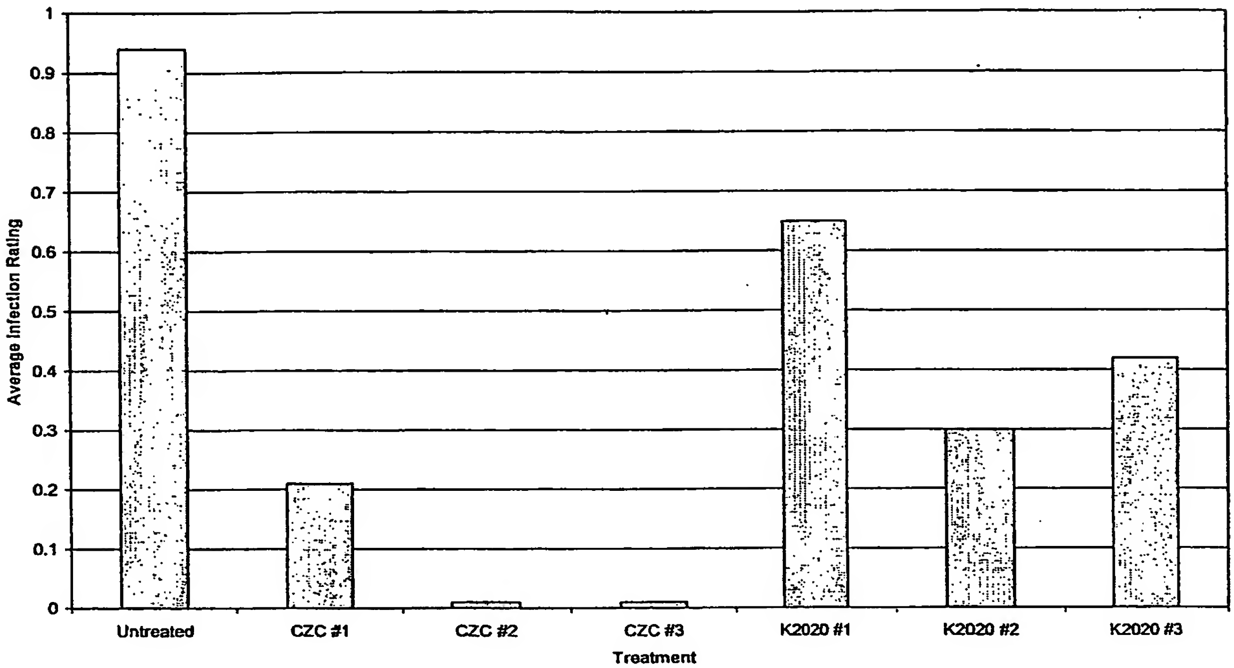

1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
Average Infection Rating
Untreated
CZC #1
CZC #2
CZC #3
K2020 #1
K2020 #2
K2020 #3
Treatment

Figure 16

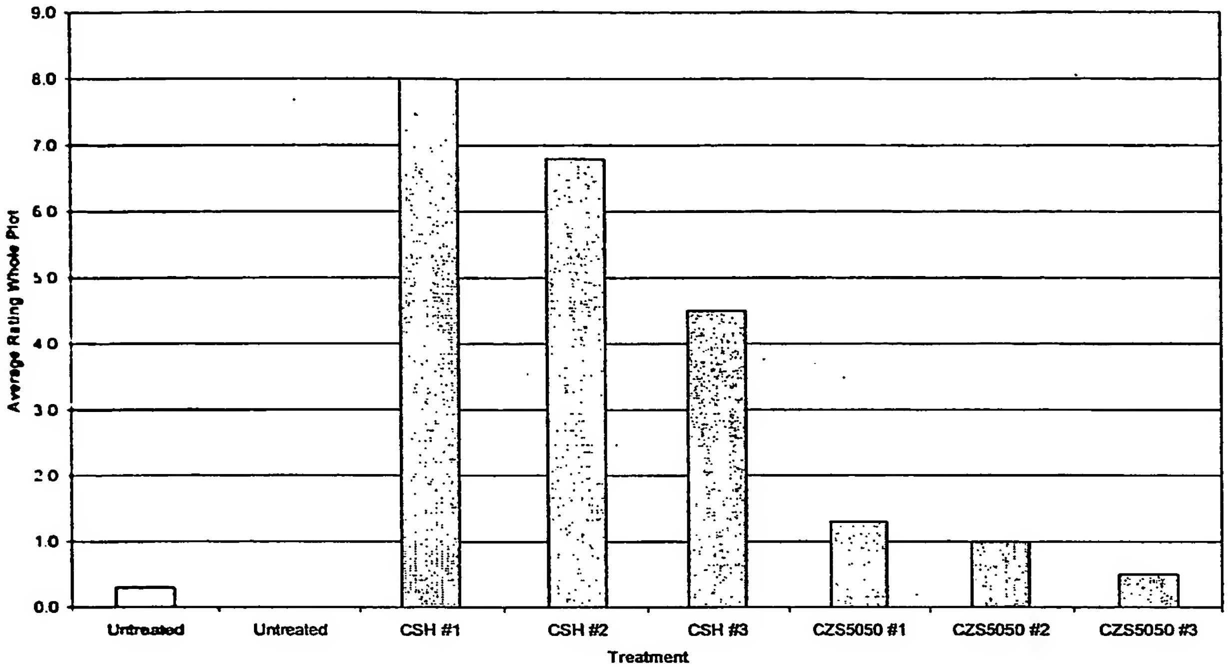

9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
Average Rating Whole Plot
Untreated
Untreated
CSH #1
CSH #2
CSH #3
CZS5050 #1
CZS5050 #2
CZS5050 #3
Treatment

Figure 17

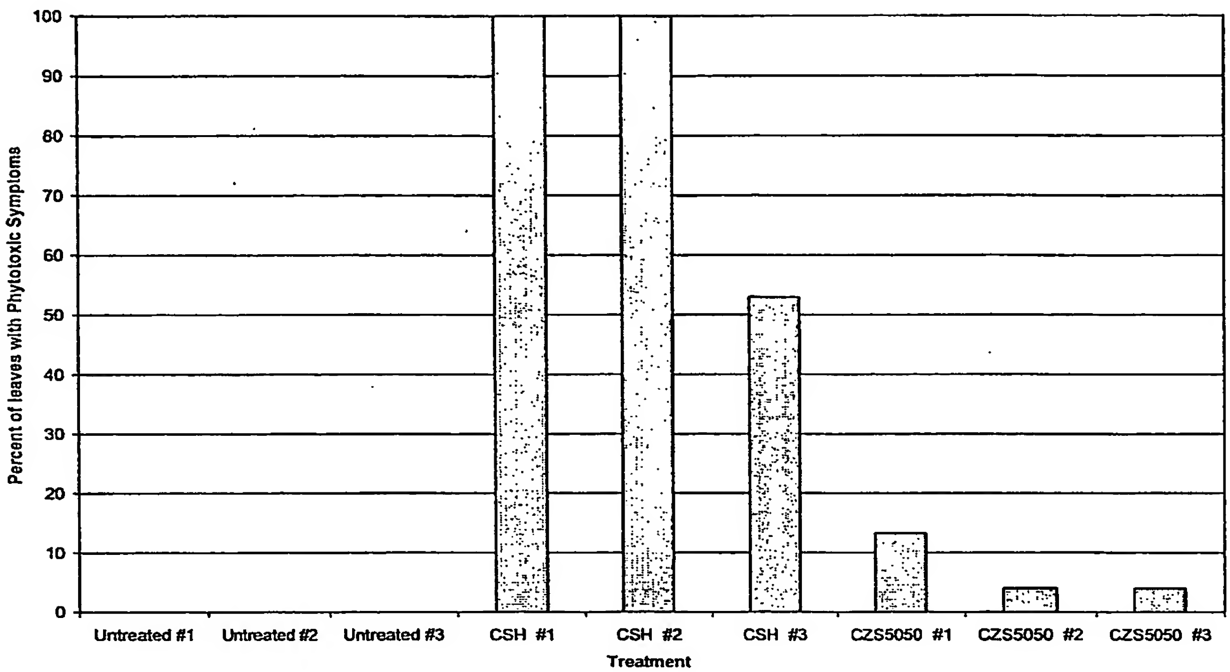
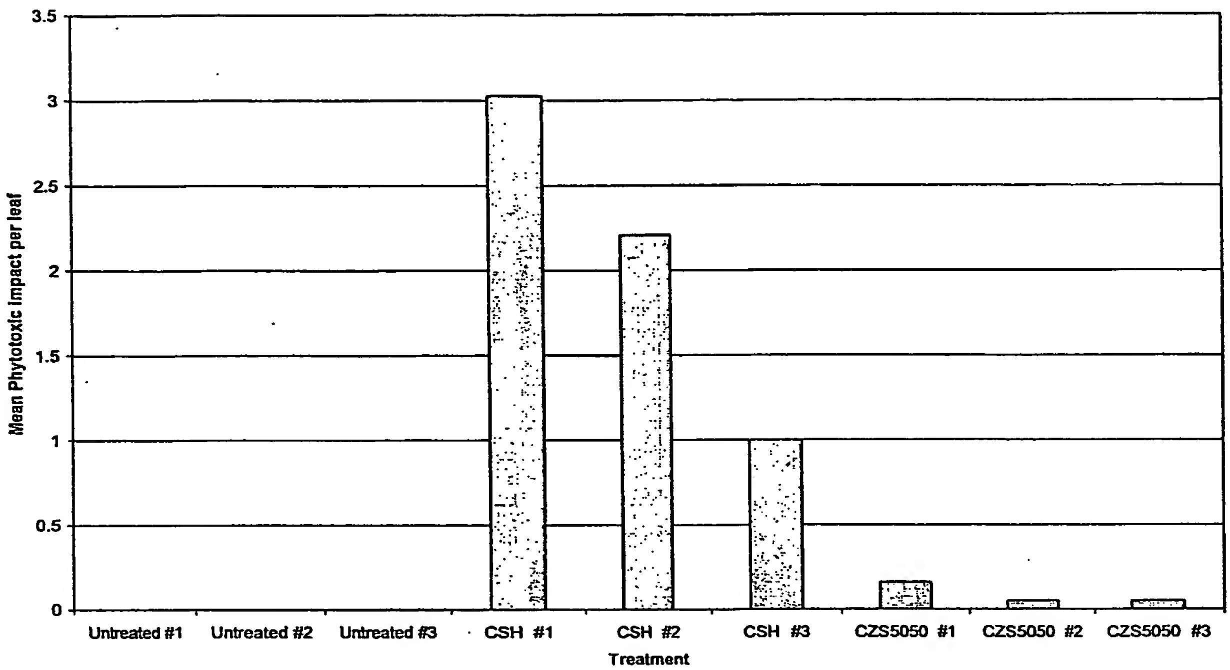

100
90
80
70
60
50
40
30
20
10
0
Percent of leaves with Phytotoxic Symptoms
Untreated #1
Untreated #2
Untreated #3
CSH #1
CSH #2
CSH #3
CZS5050 #1
CZS5050 #2
CZS5050 #3
Treatment

Figure 18


3.5
3
2.5
2
1.5
1
0.5
0
Mean Phytotoxic Impact per leaf
Untreated #1
Untreated #2
Untreated #3
CSH #1
CSH #2
CSH #3
CZS5050 #1
CZS5050 #2
CZS5050 #3
Treatment

INTERNATIONAL SEARCH REPORT

International application No.
PCT/AU03/00273

A. CLASSIFICATION OF SUBJECT MATTER

Int. Cl. [7]: A01N 59/20, 59/16; A61K 33/30, 33/34; A61L 2/16, 2/18; C01B 33/20

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
STN WPIDS, CAPLUS, Medline; keywords: zinc/Zn ; copper/Cu; silicate* .

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X,Y	WO 93/07754 A1 (SHEEN, R.J.; LANGLEY, T.A.) 29 April 1993; see page 7, third paragraph in particular. In particular note the carriers may contain zinc silicates.	1-42
X,Y	WO 99/27942 A1 (SHEEN BIOTECHNOLOGY PTY. LTD.) 10 June 1999; see the whole document, but note in particular that the potting mixes used in the examples may contain zinc silicate.	1-42
X,Y	US 6284364 B1 (SUGIZAKI ET AL.) 4 September 2001; see the whole document; see column 3, lines 24 and 34, column 7, lines 30-40.	1-2, 10-12, 23,31

[X] Further documents are listed in the continuation of Box C [X] See patent family annex

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
13 May 2003	21 MAY 2003
Name and mailing address of the ISA/AU AUSTRALIAN PATENT OFFICE PO BOX 200, WODEN ACT 2606, AUSTRALIA E-mail address: pct@ipaustralia.gov.au Facsimile No. (02) 6285 3929	Authorized officer **DAVID HENNESSY** Telephone No : (02) 6283 2255

C (Continuation).	DOCUMENTS CONSIDERED TO BE RELEVANT	
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	CN 1125513 A (WANG, Y. ET AL.) 3 July 1996; see the English abstract provided (from publicly available esp@cenet database): 'The disinfectant for increasing yield of fruit and vegetable and improving resistance of crops containing zinc sulfate, copper sulfate, surfactant and synergist and features low cost and toxicity'.	1-42
X,Y	US 5187124 A (KWEON) 16 February 1993; see column 2, line 10, column 3, lines 39-60, claims 1-7.	1-2, 10-12, 23, 31-42
X,Y	US 5151122 A (ATSUMI ET AL.) 29 September 1992; see column 1, lines 22-23, column 5, lines 5-55; discloses antimicrobial zinc/copper silicate film.	1-2, 10-12, 23, 31
Y	GB 427128 A (STANCO INCORPORATED) 16 March 1935; see the whole document; discloses a horticultural fungicide of copper silicate.	1-42
X,Y	JP 2019308 A (TOYO DORAI LE BU KK et al.) 23 January 1990; see the English abstract provided provided (from publicly available esp@cenet database); discloses an anti-microbial zinc/copper silicate film.	1-2, 10-12, 23, 31
X,Y	JP 6166513 A (CENTRAL GLASS CO LTD) 14 June 1994; see the English abstract provided (from publicly available esp@cenet database); discloses an anti-microbial zinc/copper silicate lamella structure.	1-2, 10-12, 23, 31
X,Y	JP 3193707 A (TOYO DORAI LE BU KK et al.) 23 August 1991; see the English abstract provided (from publicly available esp@cenet database); discloses anti-microbial zinc/copper silicate film.	1-2, 10-12, 23, 31
X,Y	JP 4077311 A (ASAHI KAGAKU KOUGIYOU KK) 11 March 1992; see the English abstract provided (from publicly available esp@cenet database); discloses an antibacterial zinc/copper silicate.	1-2, 10-12, 23, 31
X,Y	JP 4292410 A (TOUYOU DORAI RUUBU KK et al.) 16 October 1992; see the English abstract provided (from publicly available esp@cenet database); discloses an anti-microbial laminar zinc/copper silicate.	1-2, 10-12, 23, 31
X,Y	PRACTICAL HYDROPONICS & GREENHOUSES, vol. 54, 19-24; Morgan, L. (2000) Effect of soluble silica on hydroponic tomato crops; see the entire article, but note in particular the reference to the use of Pyrosol (TM, soluble pyrophyllite clay), which contains zinc and copper silicates, along with many other silicates, as a soluble silica nutrient.	1-31
X,Y	PRACTICAL HYDROPONICS & GREENHOUSES, vol. 47, 51-66; Morgan, L. (1999) Silica in hydroponics; see the entire article, but note in particular table 1, and the reference to pyrophyllite clays.	1-31
X,Y	PRACTICAL HYDROPONICS & GREENHOUSES, vol. 38, 14-17; Donnan, R. (1997) From a rose grower in northern New South Wales; see the entire article, but note in particular the zinc and copper nutrients would be added with potassium metasilicate.	1-42

INTERNATIONAL SEARCH REPORT

International application No.
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C (Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X,Y	PRACTICAL HYDROPONICS, vol. 10, 50-51; Diatloff, E. (1993) Silicon: beneficial element or silly con trick?; see the entire article, but note the effects on powdery mildew.	1-31
X,Y	HYDROPONIC CAPSICUM PRODUCTION: A Comprehensive , Practical and Scientific Guide to Commercial Hydroponic Capsicum Production; Morgan, L., Lennard, S.; Casper Publications, Narrabeen, NSW, Australia, 2000; Chapter 6 (Mineral Nutrition); pages 65-74; see page 70 reference to silica in particular.	1-31
X,Y	HYDROPONIC LETTUCE PRODUCTION: A Comprehensive , Practical and Scientific Guide to Commercial Hydroponic Lettuce Production; Morgan, L.; Casper Publications, Narrabeen, NSW, Australia, 1999; see Chapter 7 (Lettuce Nutrition) and Chapter 8 (Pests, Diseases and Physiological Problems); pages 75-97; see pages 77-78, 81-82, 96 references to the use of zinc, copper and soluble (pyrophyllite) silicates as a disease prevention measure.	1-31
X,Y	JP 08283013 A (MIZUSAWA CHEM. IND. CO. LTD.) 29 October 1996 & Derwent abstract accession no. 1997-017174; see the entire abstract; discloses the production of antibacterial aqueous copper silicate.	34-42

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.
PCT/AU03/00273

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report		Patent Family Member					
WO	9307754	AT	162683	AU	27621/92	DE	69224295
		DK	609285	EP	609285	ES	2111651
		GR	3026676	JP	7500326	KR	145276
		SG	47493	US	5474972		
WO	9927942	AU	16474/99				
US	6284364	JP	11010781				
CN	1125513		NONE				
US	5187124	DE	4134540	JP	6211558	KR	9400032
US	5151122	DE	4036298	FR	2654426	GB	2238044
		IL	96313	IT	1246767	JP	3218765
GB	427128		NONE				
JP	2019308		NONE				
JP	6166513		NONE				
JP	3193707		NONE				
JP	4077311		NONE				
JP	4292410		NONE				
JP	08283013		NONE				

END OF ANNEX